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Acid Mine Drainage Formation and Abatement

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27 Abstract

~~The central theme of~~ this report pertains to at-source control of pyrite oxidation. The current level of knowledge of acid mine drainage formation is critically reviewed, with emphasis on reaction kinetics and reactant and product transport. A reaction system model is developed which provides a conceptual framework for subsequent discussion dealing specifically with the physical, chemical, and biological characteristics of pyritic systems encountered in mining situations. Practical considerations of at-source control of acid mine drainage formation in underground mines, spoil banks, and refuse piles are presented in the final section ~~of the report.~~ Deficiencies in current knowledge ~~which are brought out by this report~~ include: Descriptions of the physical environment existing at pyrite oxidation sites in natural systems are far more incomplete that the current understanding of pyrite oxidation kinetics; oxygen transport is poorly described at this time, but is probably the rate-controlling factor in most instances; serious questions exist as to the effectiveness of air-sealing techniques as currently practiced; the significance of bacterial catalysis of pyrite oxidation under field conditions has not been established.

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Acid Mine Drainage Formation and Abatement

by

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1314 Kinnear Road
Columbus Ohio 43212

for the

ENVIRONMENTAL PROTECTION AGENCY

WATER QUALITY OFFICE

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ABSTRACT

ACID MINE DRAINAGE FORMATION AND ABATEMENT

The central theme of this report pertains to at-source control of pyrite oxidation. The current level of knowledge of acid mine drainage formation is critically reviewed, with emphasis on reaction kinetics and reactant and product transport. A reaction system model is developed which provides a conceptual framework for subsequent discussion dealing specifically with the physical, chemical, and biological characteristics of pyritic systems encountered in mining situations. Practical considerations of at-source control of acid mine drainage formation in underground mines, spoil banks, and refuse piles are presented in the final section of the report. Deficiencies in current knowledge which are brought out by this report include: Descriptions of the physical environment existing at pyrite oxidation sites in natural systems are far more incomplete than the current understanding of pyrite oxidation kinetics; oxygen transport is poorly described at this time, but is probably the rate-controlling factor in most instances; serious questions exist as to the effectiveness of air-sealing techniques as currently practiced; the significance of bacterial catalysis of pyrite oxidation under field conditions has not been established.

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Key Words: Acid mine water,* Pyrite,* Oxidation,* Pollution abatement,* Ferrobacillus, Strip mines, Underground mining, mine wastes

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SECTION I

CONCLUSIONS

Throughout this report, the authors have attempted to state pertinent conclusions in the appropriate chapters. In summary, we have attempted to provide a critical and quantitative description of the "real world" of acid mine drainage. The major points developed in the report are:

1. The only pyritic material in natural systems which can be oxidized at significant rates is that which is situated above the ground water table, and which is exposed to an oxygen-containing atmosphere. Pyrite which is continually submerged in a surface or ground water pool will be effectively blocked from oxygen, and no significant oxidation will occur.

2. A model has been developed which allows a quantitative description of the rate of pyrite oxidation and acid product release in terms of the physical, chemical, and biological characteristics of the system.

3. Basic chemical reaction kinetics have been established for pyrite oxidation by both O_2 and Fe^{+3}, which are the only oxidizing agents of significance in natural systems. The fundamental mechanism of pyrite oxidation has not been established. O_2, however, is the ultimate oxidizing agent in all systems.

4. Autotrophic bacteria of the Ferrobacillus - Thiobacillus group can catalyze pyrite oxidation under favorable environmental conditions. The relative significance of chemical versus biological rates in natural systems has not been established.

5. Air sealing, without elimination of breathing induced by barometric pressure changes, as is currently practiced, is not effective in giving positive control of acid production in underground mines. Mine flooding is a positive means of eliminating acid production.

6. Currently available field data are of such a nature that firm conclusions cannot be drawn as to pyrite oxidation or acid release rates, and based on these data, quantitative determinations of the effectiveness of abatement programs are questionable. Data have not been obtained which allow firm interpretations of abatement procedure effects in terms of a rational reaction system model. After application of an abatement procedure, it will be necessary to collect mine drainage data for an extended period of time, perhaps as long as five to ten years, before a sound estimate may be made of the new acid production rate. This is a result of the slow response time of natural pyritic systems to imposed changes. The slow rate of product removal from the sites of pyrite oxidation is largely responsible for this slow response. The collection of

gas-phase oxygen data from within the systems may materially reduce the time required to estimate the effect of an abatement procedure on pyrite oxidation rates.

SECTION II

RECOMMENDATIONS

The design of successful and economically feasible abatement procedures for at-source control of acid mine drainage depends on the ability to quantitatively describe rates of acid generation, and the factors controlling these rates. All pyritic systems behave in accordance with the same fundamental principles, but the individuality of each specific situation precludes the usefulness of empirical correlations and generalized qualitative conclusions. The following recommendations relate to gaps in present knowledge which present obstacles to the rational handling of real mine drainage situations.

1. A rational reaction system model should be used to bridge the gap between laboratory research and field applications. Laboratory investigations should be designed so that variable conditions which simulate the natural environment are not only controlled, but are also described in terms of physical, chemical, and biological environments, and pertinent mass transports and reaction kinetics. Conversely, field projects should be designed to allow the collection of data which can be interpreted in terms of the rational reaction system model. Because of variable hydrologic influences and slow system response to imposed changes, short-term monitoring programs should be viewed with extreme caution.

2. Mathematical descriptions of natural pyritic systems in terms of rational reaction system models should be developed for the various major types of systems. Models should relate pyrite oxidation and product removal rates to basic system characteristics. Such models will provide practical tools for the engineering design of abatement programs in abandoned, operating, and proposed mining operations.

3. The relative significance of biological and chemical rates of pyrite oxidation must be established for the various types of mining situations. Future work on abatement techniques depends significantly on this information.

4. With regard to underground mines, the development and trial of bulkhead seals and sealing techniques should be continued, and mine flooding practiced where possible. The effectiveness of air seals placed far in from the outcrop should be determined, and methods to prevent or counteract the "breathing" of air-sealed mines should be investigated. The effects of air and bulkhead seals used in conjunction with partial flooding should be investigated.

5. In the area of mine drainage treatment, emphasis should be given to the investigation of biological treatment as a possible alternative to chemical treatment.

6. Although kinetic expressions for pyrite oxidation rates have been developed, the fundamental mechanisms of these reactions have not been determined. It is recommended that efforts continue to determine basic reaction mechanisms.

SECTION III

INTRODUCTION

Within the past decade, both State and Federal authorities have become increasingly concerned about the problem of acid mine drainage. The extent to which mine drainage is impairing surface water quality has been described in recent reports[1,2] and such information will not be discussed here. It is significant, however, that affected states have established, or are establishing, more stringent regulations relating to mine drainage quality than have existed in the past. As in the case of any industrial waste, there are basically two approaches to controlling mine-acid pollution; i.e., abatement at the source, and treatment of the waste. Because acid mine drainage production has been shown to often continue unabated for scores of years following the abandonment of mining operations, treatment implies a cost that will continue for an indeterminantly long period of time. Present engineering technology, however, is sufficient to design and operate such treatment facilities. A recent report by Hill[3] discusses the state of the art and research needs of mine drainage treatment.

Abatement at the source, the ultimate alternative to treatment, is more controversial than treatment because there is serious doubt in the minds of many as to the feasibility or even the possibility of such an approach in many situations. This is particularly true in the case of abandoned underground mines. Both the abatement of acid production from abandoned operations, and the planning of existing and proposed mining operations to provide for at-source abatement, depend on the same basic principles. The understanding of these principles is incomplete, however, and there appears to be some confusion in the interpretation of laboratory and field data.

A primary purpose of this report, therefore, is to evaluate the "state of the art" of acid mine drainage at-source abatement, and to present a fundamental reaction system model which will hopefully resolve some of the conflicting concepts, and offer a sound basis for understanding, evaluating, and subsequently ameliorating the problem. An attempt is made within the present sphere of knowledge to more accurately describe and define the important physical, chemical, and biological characteristics which have a direct bearing on the rate of acid formation and acid drainage resulting from the production of coal. While this report is written with specific reference to coal mining, the principles developed apply generally to other pyritic systems.

In addition to the discussion of at-source abatement, the biological system section of this report presents a discussion of the application of biological treatment to acid drainage situations, and presents also a brief discussion of the effects of acid drainage on the ecology of receiving waters.

The report is not intended to provide an annotated bibliographical review of mine drainage literature, since this is available elsewhere.[4] It is intended instead to provide a critical analysis of the current level of understanding of the oxidation of pyritic materials in mining environments, and to define specific areas in which additional research and development is necessary to the practical solution of the problem. As the reader will see, there is disagreement in many instances between the interpretations and conclusions of the authors of this report, and other investigators active in this field. There is also some disagreement between the authors of specific sections of this report, particularly in regard to the important question of the significance of microbial catalysis of pyrite oxidation. Only through free discussion of such points will progress be made in this field, and it is hoped that this report will invite discussion, with faith in the fact that lively argument promotes lasting understanding.

SECTION IV

DEVELOPMENT OF A CONCEPTUAL MODEL FOR PYRITE OXIDATION SYSTEMS

K. S. Shumate, E. E. Smith, P. R. Dugan, R. A. Brant, C. I. Randles

It is becoming increasingly evident that much of the consideration given to acid mine drainage formation and discharge has been taken out of context. In many instances, the problem has either been oversimplified, or it has been assumed to be too complex to be handled by other than gross empirical approaches. As a result, misconceptions have been generated from time to time, and there often appears to be conflicting data between laboratory and field investigations. It is considered necessary, therefore, to present a conceptual model of pyrite oxidation for use as a frame of reference for the discussion of acid mine drainage control. This model is nothing more than a description of the reaction system, and can be readily expressed in both qualitative and mathematical terms. The pyritic system* description is intended to account for those physical, chemical, and microbial factors which influence the production (the rate of discharge of pollutants to the receiving stream) of acid mine drainage. It considers the transport of the mobile reactants (oxygen or ferric ion and water) to the pyrite, the oxidation reaction leading to the formation of oxidation products (hydrogen ion, sulfate ion, etc.), and the removal and transport of products to the system boundary (mine opening, receiving stream, etc.). This model is neither new nor controversial. Rather, it is a restatement of fundamental principles found in standard references pertinent to the description of reaction systems.

QUALITATIVE MODEL

To avoid a premature involvement with mathematical expressions, the system will first be outlined in a qualitative form. A more detailed discussion of physical, chemical, and biological considerations is given in subsequent chapters.

The oxidation of pyritic materials associated with coal and other mined minerals has often been described by the following equations:

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*The term "pyritic sytem" as used in this paper means any acid-producing situation associated with mining activity, such as gob piles, spoil banks, underground mines, etc.

$$FeS_{2(s)} + 3\text{-}1/2\ O_2 + H_2O \rightarrow 2SO_4^{=} + Fe^{+2} + 2H^{+} \qquad (1)$$

$$Fe^{+2} + 1/4\ O_2 + H^{+} \rightarrow Fe^{+3} + 1/2\ H_2O \qquad (2)$$

$$Fe^{+3} + 3\ H_2O \rightarrow \underline{Fe(OH)_3}\downarrow + 3H^{+} \qquad (3)$$

Since these are familiar to everyone involved in acid mine drainage work, it is convenient to outline the model in relation to these equations. It must be remembered that these are gross stochiometric equations, and although they indicate initial reactants and final products of oxidation, they do not define reaction mechanisms, nor do they indicate intermediate products which may cancel out of the overall equations. Further, they do not indicate all of the factors affecting the rates of each reaction, nor do they specifically indicate the locations within a given system at which the reactions take place. It is likely that the simplicity of these reactions, as they are popularly written, may itself be a factor in the tendency toward over-simplification in the analysis of pyritic oxidation systems.

Often, the three equations are added, giving the overall stochiometric relationship:

$$FeS_{2(s)} + 3\text{-}3/4\ O_2 + 3\text{-}1/2\ H_2O \rightarrow 2H_2SO_4 + \underline{Fe(OH)_3}\downarrow \qquad (4)$$

This expression does indeed identify the initial reactants, and focuses attention on the fact that sulfuric acid and ferric hydroxide are the products of the complete reaction scheme. It is the presence of these products in surface waters which is to be avoided or, at least, controlled. Once oxidation products are present in a stream, the only alternative is treatment of the drainage. This paper, however, addresses itself to the goal of abatement of pyrite oxidation at the source. In this regard, it is misleading to represent the summation of Eqs. (1), (2), and (3) in the form of Eq. (4), because this obscures the fact that the reactions 1 - 3 do not generally take place at the same location within the reaction system. Further, Eq. (1) does not represent the only possible reaction of pyrite with an oxidizing agent to yield $SO_4^{=}$, H^{+}, and Fe^{+2}. It has been conclusively demonstrated that Fe^{+3} can also be an effective oxidizing agent. To simplify the discussion at this point, the model will be developed with O_2 as the oxidizing agent which must be transported to the pyrite surface. Oxidation by Fe^{+3} will be discussed in a later section of this section, and the relative importance of the two mechanisms will be developed in subsequent sections of this report.

Referring initially to Eq. (1), several pertinent points may be drawn from fundamental considerations of this first reaction step. These points are:

1. In a natural pyritic system, the reaction shown in Eq. (1) is not at equilibrium. Pyrite in mining environments is continuously being oxidized because the system is always open, in some degree, to the entry of atmospheric oxygen. It is the rate of oxidation that determines the magnitude of the mine drainage problem, and it is therefore realistic to consider Eq. (1) in terms of rate expressions. Control of the reaction must stem from control of a rate-determining step in the reaction. Equilibrium constants merely indicate that the reaction will occur, but do not give any information as to the rate.

2. The system is heterogeneous, involving the reaction of crystalline pyrite (FeS_2) with oxygen (gaseous or dissolved in water), and water (liquid or water vapor). The reaction site is at the pyrite surface, and it is the environment at this surface which determines the rate of the reaction. This rate may be expressed in kinetic terms as a function of the concentration of reacting species. The "concentration" of FeS_2 is proportional to the surface area of the pyrite crystals, while other chemical species may be represented in conventional concentration terms, such as partial pressures (gas) or molar concentration (liquid).

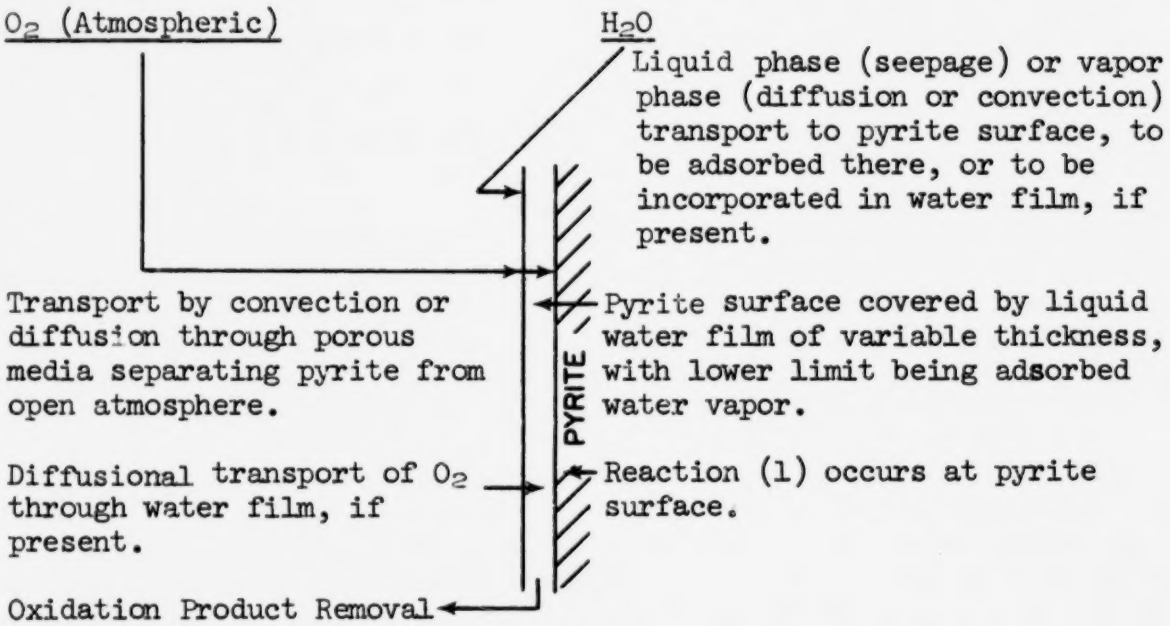
3. Equation (1) indicates that oxygen is the ultimate electron acceptor in the oxidation of pyrite, but does not necessarily imply a direct reaction of oxygen with pyritic sulfur to form sulfate. For example, it is possible that electrons may be transferred through a cyclic oxidation-reduction of iron. Such intermediates simply cancel out in the stochiometric representation in Eq. (1). Similarly, catalysis of this reaction by various possible means, particularly by bacterial action, is not reflected in Eq. (1).

4. In discussing the system it is necessary to include terms describing reaction kinetics (a function of the environment at the reaction site), and also, terms describing the rate of transport of reactants to the site. Depending on the system, either reaction kinetics or reactant transport might be rate limiting. Reaction kinetics expressions describe the resistance to reaction at the site, while reactant transport expressions describe the resistance to transport to the site. These resistances can be thought of as resistances in series, and somewhat analogous to resistances in an electric circuit. If, in a given system, either resistance is much larger than the other, it becomes the rate-limiting step, or the step which would afford the most effective control of the reaction.

5. The amount of oxygen dissolved in water entering a natural system supplies only an insignificant portion of the total demand for oxygen required at observed rates of pyrite oxidation. Therefore, to support these rates, oxygen must enter the system as a gas. Furthermore, oxygen transport within the system must also be predominantly in the gas phase, because the rate of diffusion of oxygen in water is extremely slow, and pyrite covered by more than a centimeter or two of water will be effectively shielded from exposure to oxygen. Thus, one must look to the

factors controlling gas-phase O_2 transport for a description of this major and indispensible link in the overall reaction chain.

A typical element of pyrite undergoing active oxidation might be visualized in the diagramatic form shown by Fig. 1.


O_2 (Atmospheric)
H_2O
Liquid phase (seepage) or vapor phase (diffusion or convection) transport to pyrite surface, to be adsorbed there, or to be incorporated in water film, if present.
Transport by convection or diffusion through porous media separating pyrite from open atmosphere.
Pyrite surface covered by liquid water film of variable thickness, with lower limit being adsorbed water vapor.
PYRITE
Diffusional transport of O_2 through water film, if present.
Reaction (1) occurs at pyrite surface.
Oxidation Product Removal

Oxidation products accumulate at the pyrite surface, or if a significant water film is present, they may diffuse away from site, or be carried away in seepage. However, if the thickness of the water layer separating the pyrite from the vapor phase oxygen source is on the order of a centimeter or more, oxygen diffusion through the water will be severely limited. Pyrite 'buried' below the ground water table will undergo little or no oxidation.

Fig. 1 - Pertinent Rate Processes in Acid Mine Drainage Production

These steps are put in more easily visualized form in Figs. 2, 3, and 4 which show the reaction sites, the immediate reactant and product transport environment, and the overall system environment, respectively, for a possible drift mine situation. Similar diagrams could have been drawn for a gob pile, strip pit, or any type of natural pyrite oxidation system.

Figure 2 represents the immediate vicinity of pyrite crystals undergoing active oxidation. The oxidation reaction shown by Eq. (1) occurs at the pyrite surface, at a rate dictated by conditions at that surface (O_2 concentration, nature of pyrite, etc.). As previously stated, the rate of reaction for both Case A and Case B (Fig. 2) depends on the concentrations of reactants at the point of reaction. Furthermore, oxygen must be transported to the point of reaction, and this transport requires

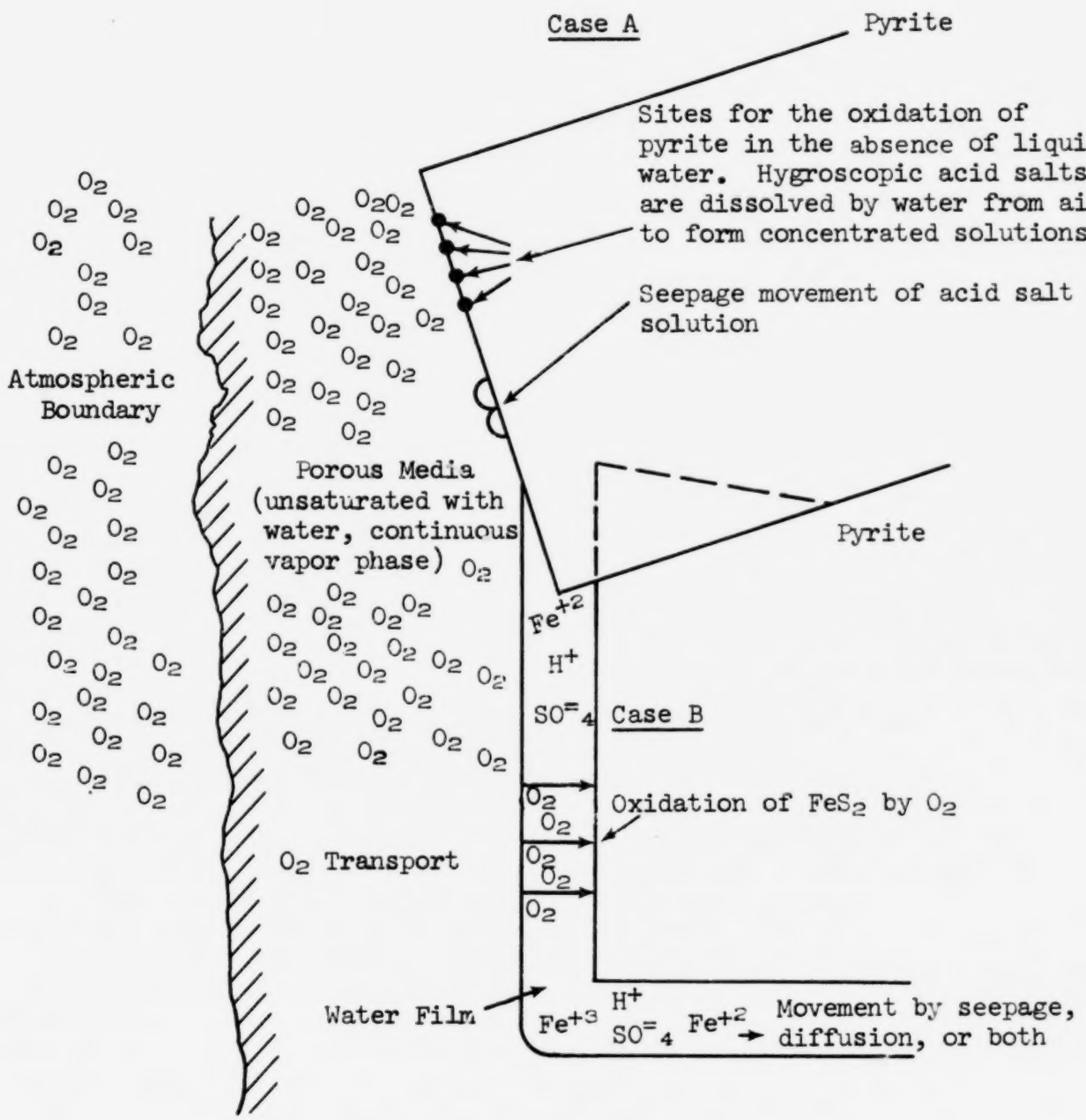


Fig. 2. Micro View of Pyritic System

an expenditure of energy. Unless there is a forced draft (convection) of air through the porous media and past the pyrite, the O_2 must move to the pyrite by molecular diffusion. If O_2 transport is by diffusion, the energy expenditure appears as a negative concentration gradient in the direction of transport. Referring to Case A, the O_2 concentration (partial pressure) at a buried pyrite surface must, in general, be less than 1/5 of an atmosphere. Only if there is convective transport of O_2 can the oxygen concentrations in the outside air and at the pyrite surface be similar. If a film of water (laminar flow seepage or stagnant film) covers the pyrite, a second energy expenditure is required to drive the diffusive transport of oxygen through the film, resulting in a second concentration drop. This applies to Case B, where the oxygen concentration at the water-vapor interface must be greater than at the water-pyrite interface. It is important to note that both reactant transport and reaction rates at the pyrite surface are concentration-dependent terms in this type of system, and are inseparably coupled. This is why it is often found convenient to draw the analogy between these two types of resistances (transport and reaction) and a simple electrical circuit with two resistances in series. Just as flow of current in a simple two-resistance circuit depends on the magnitude of both resistances, so is the rate of pyrite oxidation dependent on the magnitude of the transport and reaction resistances.

Figure 3 is a sketch of an expanded view of the sample underground mine pyrite oxidation system. This figure points out the three major factors which must be taken into account in the description of any pyrite oxidation system.

1. One must be able to describe the necessary gas-phase O_2 transport to the pyrite. This means that the O_2 concentration at the "free air" boundary, the O_2 concentration at the air-water film interface, and the O_2 concentration at the pyrite surface must all be known. The overall "driving force" of O_2 transport in the absence of convective transport* is the difference between the free air concentration and the concentration at the pyrite surface where O_2 accepts electrons from pyrite. The oxygen concentration gradient at any point determines the rate of oxygen transport through the porous media and through any water film present on the pyrite. This gradient is shown schematically in Fig. 3 as a decrease in O_2 concentration in the direction of transfer. In the case of convective transport through the porous media, the concentration drop would be primarily across the water film.

2. The concentration of O_2 at the pyrite surface determines the rate of pyrite oxidation, which under steady-state conditions must in turn be equal to the rate of oxygen transport. It should be noted that since O_2 transport must be in the gas phase through all but the last few

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*Convective transport induced by atmospheric pressure fluctuations, or "mine breathing." This will be discussed in the next section.

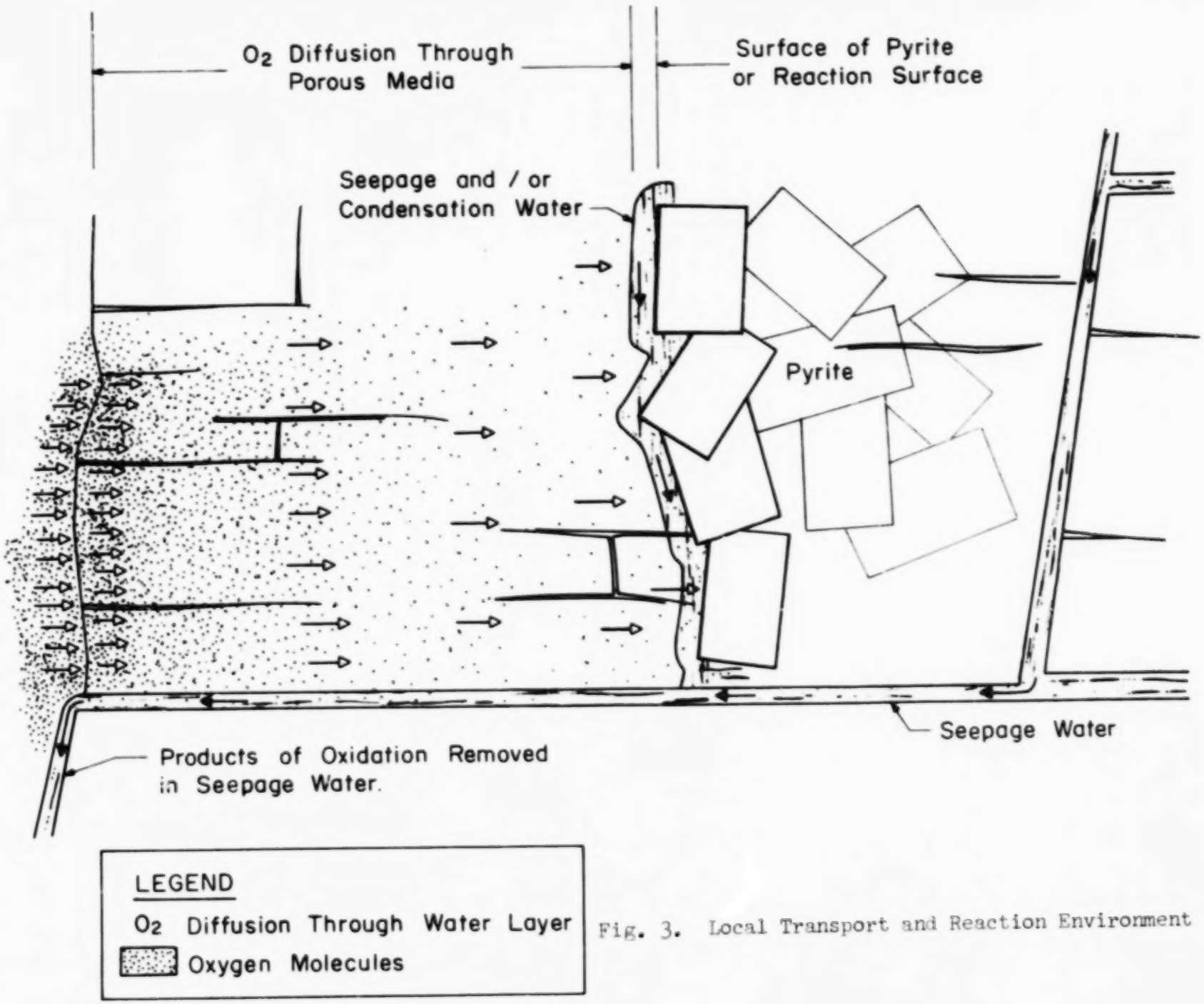

Fig. 3. Local Transport and Reaction Environment

millimeters of transport path, the amount of water in contact with pyrite is relatively small, and hence, once oxidation is initiated, pH values in this film will be quite low and salt concentrations will be quite high, approaching saturation. Chemical and biological kinetics of pyrite oxidation must conform to these conditions. The two rate processes, oxygen transport and pyrite oxidation, will adjust themselves to the conditions prevailing. They will attain equal steady-state rates, and are inseparably coupled in this manner. Depending on the system, either can be "rate controlling," and a successful abatement procedure must strike at the rate controlling process.

3. The transport process of ultimate concern is the rate of transport of oxidation products, particularly iron, H^+, and $SO_4^=$, away from the site to the receiving stream. In the situation shown in Fig. 4, the vehicle of product transport out of the system is the flowing ground water. In another situation, it might be the intermittent percolation of rain water down through the overburden. In any case, the regions of active pyrite oxidation cannot be continuously saturated with ground water, or the oxidation would be blocked because of lack of oxygen. Referring to Fig. 4, one may consider the seepage or diffusion of oxidation products as being tributary to the ground water flow. Oxidation products may either diffuse along water films to a region of active ground water flow or, because of the hygroscopic nature of these salts, they may condense water from the surrounding air to promote sufficient seepage to carry products to regions of active ground water flow. It is likely that many sites of active oxidation do not continuously contribute oxidation products at or near the site. When an intermittent flow of percolating rain water or a rising ground water table approaches or intersects the region of product storage, there will be a surge of acid products from the system. This is regularly noticed in many instances during the spring increases in ground water flow. Even though many oxidation sites may be flooded out during such a period, and the total rate of pyrite oxidation may be at a minimum, the rate of transport of products out of the system might be at its maximum. It is important to note that the two processes (oxygen transport and pyrite oxidation kinetics) which control the rate of pyrite oxidation cannot at this time be directly measured in natural systems. One must examine effluent drainage and, from this, attempt to infer the extent and rate of pyrite oxidation. Because of the intermittent and unpredictable nature of this product removal mechanism, inferences as to effects of abatement procedures on oxidation rates must be made with considerable caution.

Returning to equations 2 and 3, locations within the system at which these reactions might occur can be defined. It was indicated above that oxidation-reduction of the Fe^{+2} - Fe^{+3} couple is very likely a link in the electron transport chain leading to oxidation at the pyrite surface. However, the drainage from a site of pyrite oxidation is not likely to contain much iron in the Fe^{+3} form (because of the slow rate of Fe^{+2} oxidation in acid solution and the rapid rate of Fe^{+3} reduction at the pyrite surface) unless bacterial action can catalyze the oxidation

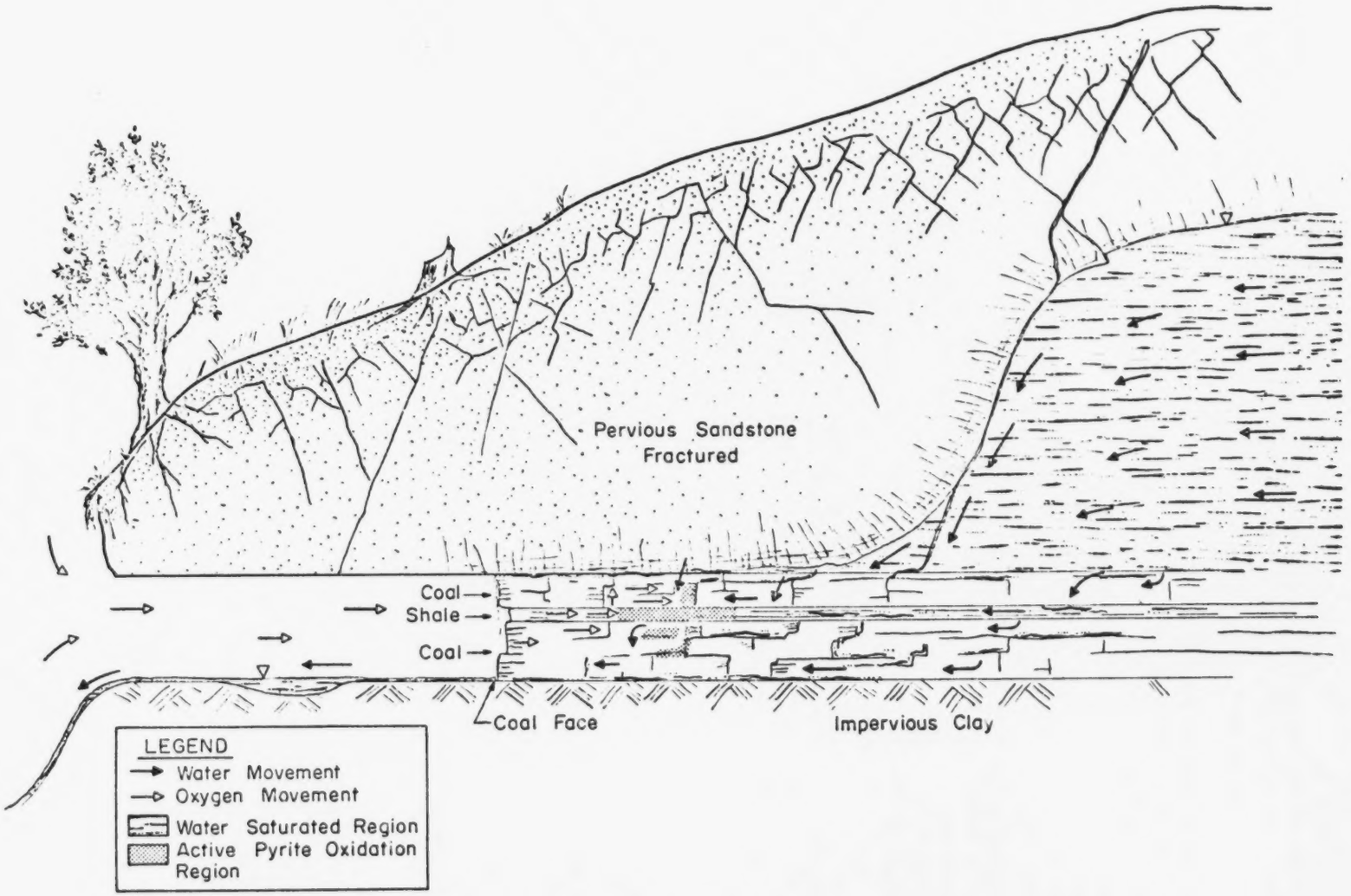

Fig. 4. General Underground Mine Environment

rate of Fe^{+2} to Fe^{+3}. It should be noted that such catalysis has not yet been directly observed in a natural environment, where the active regions cannot be saturated with water, although the numbers of organisms found in some drainages may indicate that catalysis occurs.

After Fe^{+2} ion is transported away from the site of oxidation, and mixed with ground waters which may raise the pH, the rate of $Fe^{+2} \rightarrow Fe^{+3}$ oxidation may be greatly increased. The growth of bacteria, particularly in pooled water exposed to oxygen, as on the floor of a mine, may result in almost complete conversion of Fe^{+2} to Fe^{+3} in the drainage before it leaves the mine. The soluble iron at the site of oxidation, however, may be essentially all in the Fe^{+2} state. The characteristic "yellow boy" precipitate formed by the reaction shown in equation 3 is dependent on both Fe^{+3} concentration and on the pH, the reaction becoming more complete as pH increases toward neutrality. Both reactions 2 and 3 may begin to occur at the site of oxidation, but will not proceed in large degree until the concentrated acid seepage is diluted with ground water and the pH begins to rise. The reactions may become very pronounced as diluted acid flows along the floor of the mine, and will go essentially to completion in the receiving waters below the mine. However, oxidation and precipitation reactions which occur after the strong acid solution leaves the pyrite and finds its way to flowing ground water will have no effect on the rate of pyrite oxidation unless additional pyrite is contacted along the way.

QUANTITATIVE MODEL

Reaction Rates

For purposes of demonstration, the model will be developed for the specific case outlined in the figure below, and assuming Eq. (1) to be the predominant pyrite oxidation reaction. Again, this limitation of the pyrite oxidation reaction to the case of direct oxidation by O_2 is done only to simplify presentation of the model.

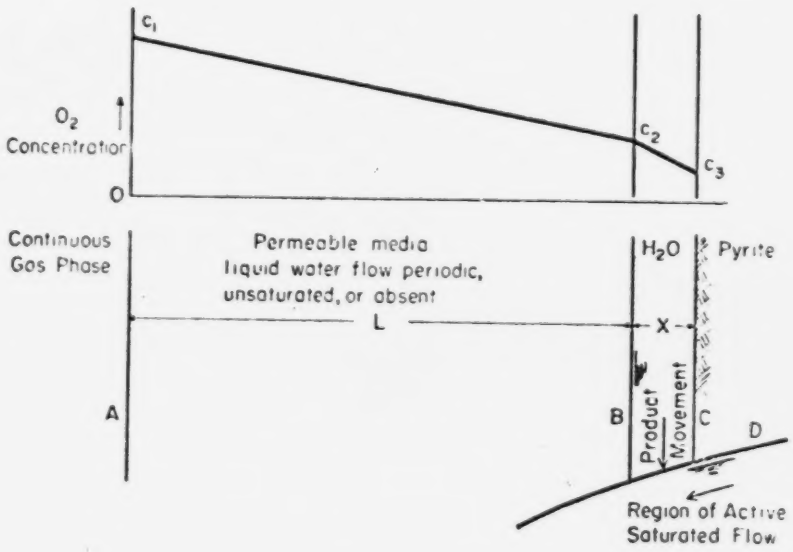

Fig. 5. Simplified Model of Pyritic System

Here, it is assumed that the oxygen concentration c at the porous media boundary A is c_1, that oxygen transport through the porous media is by diffusion only (no convective transport), that a water film covers the pyrite, and that the pyrite is oxidized directly by O_2 at the pyrite surface. Working with a unit area of pyrite,

$$r_r = k_1 c_3^n \quad , \tag{5}$$

where

r_r = rate of reaction (moles O_2/hr consumed),
k_1 = reaction rate constant,
c_3 = O_2 conc. at pyrite surface, and
n = apparent order of reaction.

To simplify this example, it will be assumed that n = 1. At steady state,

$$r_r = r_{t_1} = r_{t_2}, \tag{6}$$

where

r_{t_1} = rate of O_2 transport through porous media (moles O_2/hr)

and

r_{t_2} = rate of O_2 transport through water film (moles O_2/hr).

Further, $r_{t_1} = \frac{D_1}{L}(c_1 - c_2)$ and $r_{t_2} = \frac{D_2}{X}(c_2 - c_3)$, (7)

where D_1 = diffusivity of O_2 through the porous media,

D_2 = diffusivity of O_2 through the water,

L = length of diffusion path through porous media,

X = length of diffusion path through water film,

c_2 = O_2 conc. at porous media - water film interface, and

c_3 = O_2 conc. at pyrite surface.

Rearranging Eqs. (7)

$$c_1 - c_2 = \frac{L}{D_1} r_{t_1} = \frac{L}{D_1} r_r$$

and (8)

$$c_2 - c_3 = \frac{X}{D_2} r_{t_2} = \frac{X}{D_2} r_r \quad .$$

Adding Eqs. (8)

$$c_1 - c_3 = r_r \left(\frac{L}{D_1} + \frac{X}{D_2}\right)$$

and (9)

$$r_r = \frac{1}{\frac{L}{D_1} + \frac{X}{D_2}} (c_1 - c_3) \quad .$$

Note that for a given value of $c_1 - c_3$ (the overall driving force for oxygen transfer) an increase in L or X, or a decrease in D_1 or D_2, will lead to a decrease in r_r. However, for a given oxidation site in a given system, L, X, D_1, and D_2 will be constant and Eq. (9) may be rewritten as

$$r_r = k_m (c_1 - c_3) \quad , \tag{10}$$

where k_m is the overall oxygen transfer coefficient for the system. Combining Eqs. (5) and (10) [with n = 1 in Eq. (5)]

$$k_1 c_3 = k_m (c_1 - c_3)$$

or

$$c_3 = \frac{k_m}{k_1 + k_m} c_1 \tag{11}$$

This gives the oxygen concentration at the pyrite surface in terms of the concentration of oxygen at the outside atmospheric boundary A, the mass transport characteristics of the system (k_m), and the kinetic rate constant (k_1).

Rearranging Eq. (11)

$$k_1 c_3 = \left[\frac{k_1 k_m}{k_1 + k_m} \right], c_1$$

$$k_1 c_3 = \left[\frac{1}{1/k_m + 1/k_1} \right] c_1$$

and

$$r_r = \left[\frac{1}{1/k_m + 1/k_1} \right] c_1$$

Thus, the rate of oxidation may be expressed as a function of k_m, k_1, and the concentration of oxygen at the outside atmospheric boundary of the system c_1. This is analogous to a simple electrical circuit with two resistances, R_1 and R_2, in series, in which case

$$I = \frac{1}{R_1 + R_2} E \quad ,$$

where I = current flow and E = potential drop.

In looking at the problem in the manner shown above, it is not necessary to assume a first-order reaction as shown in Eq. (5), nor is it necessary to assume a single site with single values of L and X.

This was done only to simplify this example. The model can be expanded to fit complex situations, with the major limitation being valid data on the factors determining mass transport and kinetics. For example k_m is a function, in general, of the scale of the system, the number of sites, and of the factors determining both molecular diffusion and convective transport of oxygen, and of the electron transport intermediates in the water film, if present. Similarly, k_1 is a function of oxygen, ferrous, and ferric ion concentrations at the pyrite surface, the nature and surface area of the exposed pyrite, and catalytic factors such as bacterial activity. All of these factors must be accounted for in a description of the reaction system.

In any specific case, either mass transport or kinetics might be the rate-determining factor, depending on the relative values of k_1 and k_m. For example, take the case where r_t (rate of O_2 transport) $= k_m (c_1 - c_3)$, and $r_r = k_1 c_3$. As before, $r_r = r_t$, and the simultaneous solution of the expressions for r_t and r_r will yield the rate of transport (or of reaction) and the concentration of oxygen at the pyrite surface which will be maintained at steady state. This solution, which was carried out analytically above, is demonstrated graphically below.

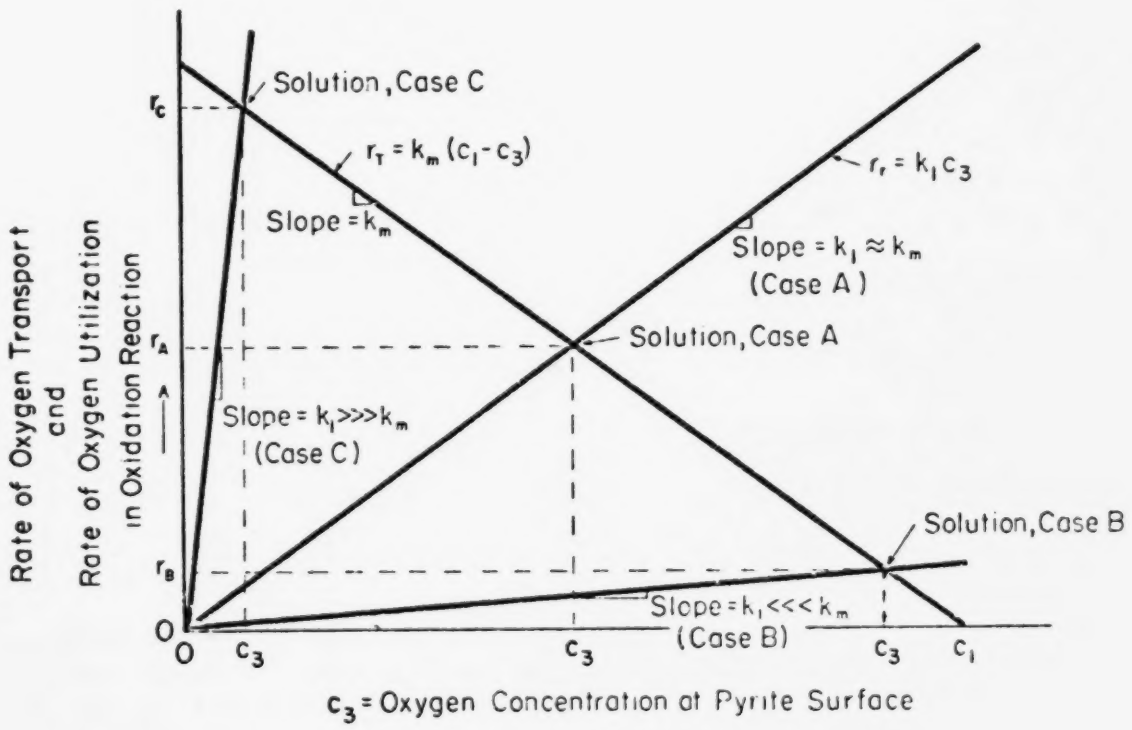

Fig. 6. Solution and Steady State Rate Equation

Three cases are shown: Case A, $k_1 \approx k_m$; Case B, $k_1 <<< k_m$; and Case C, $k_1 >>> k_m$.

In Case A, it is seen that a change in either k_1 or k_m will yield a significant change in the steady-state reaction rate; that is, both are rate controlling. In Case B, the steady-state reaction rate is very sensitive to changes in k_1, but is insensitive to changes in k_m; thus, the kinetics are rate controlling. The reverse is true in Case C, where mass transport is rate controlling. To control pyrite oxidation at the site, we must direct our efforts toward the control of the rate-controlling step, which will vary from one situation to another. It is the ultimate effect of such procedures as mine sealing on the rate-controlling step which is of importance. A description of pyritic systems as a rational reaction system provides a rational tool for the abatement of pyrite oxidation at the source.

EXTENSION OF REACTION RATE MODEL TO ACCOUNT FOR PYRITE OXIDATION BY FERRIC IRON

It was stated above that both O_2 and Fe^{+3} are potential oxidizing agents of pyrite in natural systems. Rewriting Eq. (1) in more general terms,

$$FeS_2(s) + \text{electron acceptor} \rightarrow Fe^{+2} + 2S(VI) + \text{reduced electron acceptor} \qquad (12)$$

If ferric iron is the electron acceptor, then the pyrite oxidation reaction may be rewritten as

$$FeS_2(s) + 14\ Fe^{+3} + 8H_2O \rightarrow 15Fe^{+2} + 2SO_4^{=} + 16H^{+} \quad . \qquad (13)$$

The only available supply of the ferric iron required in this reaction is through the continuous reoxidation of ferrous iron by oxygen, as shown in Eq. (2). Rewriting Eq. (2) to show the oxidation of 14 moles of Fe^{+2},

$$14Fe^{+2} + 3\text{-}1/2\ O_2 + 14H^{+} \rightarrow 14Fe^{+3} + 7H_2O \qquad (14)$$

Adding Eqs. (13) and (14) gives the overall reaction

$$FeS_2(s) + 3\text{-}1/2\ O_2 + H_2O \rightarrow Fe^{+2} + 2SO_4^{=} + 2H^{+} \quad . \qquad (15)$$

Equation (15) is identical to Eq. (1) and by either path (O_2 or Fe^{+3} oxidation) the net reaction is the same. In both cases, oxygen must be supplied to the system at a rate equivalent to the rate of pyrite oxidation. The important difference lies in the fact that if pyrite is oxidized by oxygen, O_2 must be continuously supplied at the pyrite surface, while for oxidation by ferric iron, ferric iron must be continuously supplied. For the continuous steady-state reaction, rates of transport and reaction are related by the following expressions:

Oxygen Oxidation

Rate of O_2 transport to pyrite surface = Rate of pyrite oxidation by O_2

Ferric Iron Oxidation

Rate of O_2 transport to water overlying FeS_2 = Rate of oxidation of Fe^{+2} to Fe^{+3} by O_2 (bacterially catalyzed) = Rate of Fe^{+3} transport to pyrite surface = Rate of oxidation of pyrite by Fe^{+3}

A model description of the latter system (ferric oxidation) differs from the oxygen oxidation system only in that two transport steps and two reaction kinetics terms must be accounted for, rather than one transport step and one reaction kinetics term. Mass transport and reaction kinetics will be specifically discussed in subsequent chapters.

ACID PRODUCT RELEASE RATES

Just as reaction rates can be modeled rationally, so also can product release rates be similarly modeled. Referring to Fig. 5, products of oxidation will move away from the site by either diffusion or convection, depending on whether the water film on the pyrite is moving or stagnant. If there is no water film, the products will remain at the site. The rate and frequency with which the products are removed from the system will depend on the mechanism of transport away from the site, and the relative position of flowing ground water. As ground water levels rise, they will flush out products held near the site, or moving very slowly in the vicinity of the site. It is significant to note that rising ground water may "flood out" oxidation sites, temporarily decreasing the rate of oxidation, but at the same time, the rate of removal of oxidation products from the system may be a maximum value. The overall process of product removal can be adequately represented by well-established expressions describing mass transport and ground water flow. The primary factor to bear in mind is the fact that the distance from the site to a region of active ground water flow is variable with time and will vary with changing ground water patterns.

VALUE OF MODEL

It is believed that through the description of pyrite oxidation systems in the context of the model presented above, the discussion of such systems will become clearer and problems of communication can be considerably lessened. This model provides a basic framework for the discussions in the following sections of this report, and, it is further

hoped that it will have a clarifying influence on the general understanding of pyrite oxidation in "natural" systems. This same type of model has similar applications to other heterogeneous reaction systems.

SECTION V

THE PHYSICAL SYSTEM

K. S. Shumate and R. A. Brant

In the previous section, pyritic systems were discussed in the context of generalized reaction systems. The purpose of this section is to discuss the physical characteristics of pyritic systems which have an important influence on the rate of pyrite oxidation. In order to set the stage for this discussion several previously mentioned fundamental characteristics are re-emphasized below.

First, if pyrite is to be oxidized continuously, then all reactants must be continuously made available at the reactive site; i.e., the pyritic surface. In natural systems, the reactants are H_2O, FeS_2, and an oxidizing agent which can be either O_2 or Fe^{+3} ion. The FeS_2 is immobile, and initially present in the system, with the total amount of FeS_2 representing the total reaction capacity of the system. H_2O is present in sufficient quantity in any damp environment in which there is liquid water, or relative humidities approaching 100%. The oxidizing agent, whether it be O_2 or Fe^{+3}, is not initially present in the system in appreciable quantities, and if it is not continuously supplied, the reaction will soon stop. Further, the only source of Fe^{+3} is through the oxidation of Fe^{+2} released from the pyrite, and O_2 is the only available oxidizing agent which can accomplish this reaction. Therefore, regardless of the oxidizing agent which is active at the pyrite surface, O_2 must be continuously supplied to the system at a rate chemically equivalent to the rate of pyrite oxidation. Since the amount of oxygen which can enter the system as oxygen dissolved in water is insignificant when compared to the amounts of oxidation products commonly observed in acid drainages, it follows that effectively all of the oxygen taking part in the overall reaction must enter the system in the gas phase.*

MECHANISMS OF O_2 TRANSPORT

There are only two mechanisms by which O_2 can be transported; i.e., convective transport and molecular diffusion. With regard to the former mechanism, there are three major possibilities for the generation

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*In accordance with Eq. (4), the reaction of 1 mg O_2 with pyrite will produce 1.67 mg acidity, as $CaCO_3$. The saturation value of dissolved oxygen in water is approximately 9 mg/ℓ. Therefore, oxygen dissolved in water before the water contacts the pyrite can account for, at the most, approximately $9 \times 1.67 = 15$ mg/ℓ acidity.

of significant oxygen movement. First, and most obvious, would be the continuous renewal of O_2 at the surface of a spoil bank or refuse pile by wind currents. Because of the slow rate of the pyrite oxidation reaction, little air movement would be necessary to maintain atmospheric oxygen concentrations at pyritic surfaces directly exposed to the atmosphere.

A second potentially important source of air movement applicable to underground mines would be the effective ventilation of significant mine volumes by thermal convection currents, generated by temperature differentials inside and outside the mine. In this case, pyritic materials exposed at the surface within the mine could be continuously supplied with oxygen.

The third significant mechanism for the generation of convective transport is the "breathing" of any semi-confined gas volume due to fluctuations in atmospheric pressure. The principle is most readily expressed in terms of the ideal gas law,

$$Pv = nRT \quad ,$$

where

P = absolute pressure,
v = gas volume,
n = number of moles of gas in volume v,
R = universal gas constant, and
T = absolute temperature.

Rewriting this expression in differential form, with v, R, and T held constant,

$$dn/dP = v/RT = \text{constant},$$

or, the number of moles of gas which must enter or leave any semi-confined (vented) gas volume during a given pressure fluctuation is directly proportional to the volume.

This volume might be the interconnected pore spaces in a gob pile or spoil bank, or the mined volume of an underground mine. Since atmospheric pressure fluctuations of one per cent or more (per cent of absolute pressure) over a few days time are not uncommon, refuse piles and underground mines will breathe one per cent or more of their vented gas volumes in and out during these periods. An atmospheric pressure increase will force outside atmosphere into the system, and an atmospheric pressure decrease will draw mine atmosphere out. If the vented, semi-confined gas volume is large, this can result in a significant amount of oxygen transport. Further, if pyritic material lies along the vent pathways or in the region to which gas is continually being supplied or removed, it will have access to a more or less continuous supply of oxygen.

It should be noted that convective transport is a transfer mechanism which is applicable to any fluid system, either gaseous or liquid. However, in mining situations, convective transport need only be considered as it applies to the gas or vapor phase. The only liquid phase present is adsorbed water vapor, stagnant water films overlying the pyritic surfaces, or slowly seeping ground water. In all cases, the water is either not flowing, or undergoing laminar flow, and there is no turbulent mixing in the water phase. Therefore, any movement of O_2 across the water barriers separating the pyritic surfaces from O_2 in the vapor phase must be by molecular diffusion, and will occur whenever there is a concentration gradient of O_2 through the water layer. Similarly, molecular diffusion of O_2 through a mixture of gases will always occur whenever there is an O_2 concentration gradient. When dealing with molecular diffusion in any fluid phase, the rate of O_2 transport can be represented by the expression:

$$\frac{N}{A} = -D \frac{dc}{dx} \qquad (16)$$

where

N = rate of O_2 transport, $\frac{\text{gram moles}}{\text{hr}}$,

A = cross sectional area of fluid normal to the direction of transport, cm^2,

$\frac{dc}{dx}$ = concentration gradient of O_2 in the fluid along the direction of transport, $\frac{\text{gram moles } O_2}{cm^3 - cm}$; transport is in the direction of the negative concentration gradient, or in the direction of decreasing concentration, and

D = coefficient of diffusivity, $\frac{cm^2}{hr}$.

It is seen that for a given concentration gradient $\frac{dc}{dx}$, the rate of transport per unit area $\frac{N}{A}$ is directly proportional to the diffusivity D. The magnitude of this coefficient is strongly dependent on the nature of the fluid phase, being generally much higher in gases than in liquids. For example, for the diffusion of O_2 through air at 25°C and 1 atm pressure, $D = 0.206 \frac{cm^2}{sec}$. For the diffusion of O_2 through water at 25°C, $D = 0.18 \times 10^{-4} \frac{cm^2}{sec}$. Thus, the diffusivity of O_2 in air is slightly more than 10,000 times as great as the diffusivity of O_2 in water. Water, however, is a more efficient diffusion barrier to the transport of O_2, as compared to air, by a factor of more than 10,000, because of the low solubility of O_2 in water. For example, take a water film 1 mm thick, exposed to air on one side and pyrite on the other; let the dissolved oxygen concentration on the air side be saturated with O_2

at 9 mg/ℓ and let the dissolved oxygen at the pyrite surface be 4.5 mg/ℓ Under these conditions, using the diffusivity given above,

$$\frac{dc}{dx} = \frac{(4.5-9)\ \frac{mg}{\ell} \times \frac{1}{32 \times 10^3}\ \frac{\text{gram moles}}{mg} \times \frac{1}{10^3}\ \frac{\ell}{cm^3}}{0.1\ cm} \quad ,$$

$$\frac{dc}{dx} = - \frac{4.5}{32 \times 10^5}\ \frac{\text{gram moles}}{cm^4} \quad ,$$

and

$$D = 0.18 \times 10^{-4}\ \frac{cm^2}{sec} \times 3.6 \times 10^3\ \frac{sec}{hr} = 0.648 \times 10^{-1}\ \frac{cm^2}{hr} \quad ;$$

therefore,

$$\frac{N}{A} = - (0.648 \times 10^{-1}) \times \frac{4.5}{32 \times 10^5} \approx 1 \times 10^{-7}\ \frac{\text{gram moles}}{hr - cm^2} \quad .$$

Now, consider pyrite covered by a stagnant layer of air 1 mm thick. Let the oxygen concentration at the outside boundary of the air layer be 20 per cent, which is approximately the chemical equivalent of 9 mg/ℓ of O_2 dissolved in water (air at 1 atm pressure, 20 per cent oxygen, and 25°C is an equilibrium with about 9 mg/ℓ O_2 dissolved in water). Further, let the oxygen concentration at the air-pyrite interface equal 10 per cent, approximately equivalent to 4.5 mg/ℓ dissolved oxygen in water. Under these conditions, and using an oxygen diffusivity in air of 0.206 cm^2/sec, the rate of O_2 transport across the 1 mm air layer is calculated by Eq. (16) as approximately 3×10^{-2} gram moles/hr-cm^2, or 3×10^5 times as great as in the case of diffusion through a 1 mm water layer. Similarly, if the stagnant air layer is 300 meters thick, with an oxygen drop across the layer from 20 per cent to 10 per cent, the rate of oxygen transport would be approximately 1×10^{-7} gram moles/hr-cm^2, or the same as the 1 mm water layer. Thus, one can consider water (stagnant, or in laminar flow) to be 300,000 times more effective than stagnant air as a barrier to oxygen diffusion.

In the case of oxygen diffusion into a water film, with bacterial catalysis of Fe^{+2} to Fe^{+3}, and transport of Fe^{+3} to the pyrite surface to drive the oxidation of pyrite (see page 21), diffusion rates become more difficult to analyze because of the complexity of the system. However, molecular diffusion rates for iron ions in water are of the same order of magnitude as for oxygen, and the extreme effectiveness of water as a diffusion barrier for any electron acceptor, whether it is O_2 or Fe^{+3}, must still be considered.

EFFECT OF WATER FILM THICKNESS

In order to provide a feeling for the effect of varying water layer thickness on the rate of oxidation of pyrite, consider one gram of pyrite exposed to air (20 per cent O_2) and having a relative humidity of 100 per cent. Assume that the rate of oxygen utilization in pyrite oxidation is 15 μg per hour per gram (a reasonable rate for finely divided sulfur ball material), and that the effective cross sectional area for O_2 transport to the pyrite is 10 cm^2. If the pyrite is then covered with water and agitated, the dissolved oxygen throughout the water will approach saturation, and the oxidation rate will remain at 15μg per hour*. However, there is no agitation of water layers in a mining situation, so the only O_2 transport to the pyrite is by molecular diffusion. Consider first a 1-mm water layer over the pyrite (either a quiescent or laminar flow layer). Assume that the rate of oxidation of pyrite is directly proportional to the oxygen concentration at the pyrite surface.** Then

$$W = kc_2' \qquad (17)$$

where

c_2' = O_2 concentration at the pyrite surface (mg/ℓ), and

W = rate of oxygen utilization (μg/hr).

Assuming the saturation dissolved oxygen value at 20 per cent oxygen is 9 mg/ℓ, then when c_2' = 9 mg/ℓ, W = 15 μg/hr.

Therefore, for this system, $k = \frac{15}{9} = 1.67$. The diffusivity of oxygen in water is approximately $1.8 \times 10^{-5} \frac{cm^2}{sec} = 6.48 \times 10^{-2} \frac{cm^2}{hr}$, and

$$\frac{N}{A} = -D \frac{dc}{dx} \qquad (16)$$

where $A = 10\ cm^2$,

$N = \frac{\text{gram moles } O_2}{hr}$,

$D = 6.48 \times 10^{-2} \frac{cm^2}{hr}$,

and

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* Smith[5] has shown that for the oxidation of pyrite by oxygen, the oxidation rate for pyrite exposed to air at a given oxygen content is the same as for pyrite exposed to water saturated with oxygen with respect to the given air oxygen content.

**An oversimplification, but close to that observed for the oxidation of pyrite by oxygen, and sufficiently accurate for the purpose of this example.

$$c = \frac{\text{gram moles } O_2}{cm^3} \quad .$$

1 gram mole of O_2 = 32×10^6 µg, so $N = \frac{W}{32 \times 10^6}$;

also 1 gram mole = 32×10^3 mg, so $c' \frac{mg}{\ell} = c' \times 10^{-3} \frac{mg}{cm^3} = 32 \times 10^3 \, c \frac{mg}{cm^3}$,

and

$$c = \frac{c'}{32 \times 10^3}$$

Therefore, substituting into Eq. (16),

$$\frac{W}{10} = - D \frac{dc'}{dx} = \frac{-D(c_2' - c_1')}{0.1}$$

where c_2' = O_2 concentration in mg/ℓ at the pyrite surface and c_1' = O_2 concentration in mg/ℓ at the air-water film interface.

Rearranging,

$$W = 10^2 \times Dc_1' - 10^2 \times Dc_2' \quad .$$

If we assume that the outside of the film is saturated with oxygen (with respect to air at 20 per cent O_2) at a value of 9 mg/ℓ, then c_1' = 9 mg/ℓ,

and

$$W = (10^2 \times 6.48 \times 10^{-2} \times 9) - (10^2 \times 6.48 \times 10^{-2} \, c_2'). \quad (18)$$

This is the transport rate, which, at steady state, must also be equal to the O_2 utilization rate

$$W = 1.67 \, c_2'$$

or

$$c_2' = \frac{W}{1.67} \quad . \quad (19)$$

Combining Eqs. (18) and (19), and solving for W,

$$W = 58.3 - \frac{6.48W}{1.67} \quad (20)$$

and

$$W = \frac{58.3}{4.89}$$

or

$$W = 11.9\ \mu g/hr \quad .$$

Thus, with a 1-mm film of water, the oxidation rate has dropped significantly from 15 μg/hr (no water film) to 11.9 μg/hr.

If the film is increased to a thickness of 1 cm, then Eq. 20 becomes

$$W = 5.83 - \frac{0.648W}{1.67}$$

or

$$W = \frac{5.83}{1.39} = 4.2\ \mu g/hr \quad .$$

Similarly, a 2-cm thick overlying layer results in an equilibrium rate of 2.4 μg/hr, and a 10 cm thickness of overlying water decreases the rate to 0.56 μg/hr, or less than 4 per cent of the rate with no overlying water film.

In the case of the bacterially catalyzed oxidation of Fe^{+2} to Fe^{+3} in the water film and oxidation of the pyrite by Fe^{+3}, the calculation of water layer effect becomes much more complex. However, the mobile electron acceptors, O_2 and Fe^{+3}, still must move through the water by diffusion, and the overall effect will be similar.

It should be noted that the above calculations are sensitive to the value assigned to the effective transport area, or to the available transport area per gram of exposed pyrite. The authors feel that the value assigned is reasonable, but there is no direct confirmation of this assumption.

Generally speaking, as the effective transport area A per unit of pyrite activity decreases, the effectiveness of the water film as an oxygen barrier increases. For example, if a transport area of less than 10 cm^2 were available to carry oxygen to the pyrite in the above example, the equilibrium oxidation rate would be less than the values shown above for the various film thicknesses.

PHYSICAL CHARACTERISTICS OF MAJOR MINE TYPES

Natural pyritic systems may logically be separated into two categories: (a) Situations in which the pyrite is largely left in place, but is exposed to oxidizing environments, (e.g., underground mines); and (b) relocated materials, which includes both spoil piles and refuse piles. A physical characterization of any type of pyritic system, however, must include the following basic information:

1. Type and location of pyritic material.

2. Location of zones where pyrite is submerged below the free water surface of pooled water or bodies of ground water, in which case the pyrite is sealed off from oxidation.

3. Nature and location of underground water flow patterns, which provide the vehicle for removing oxidation products from the system.

4. Physical characteristics of the structure surrounding exposed* pyrite, which determine the availability of O_2 to pyrite by either convective transport or molecular diffusion.

The various types of mining situations differ widely in these respects, and representative types will be discussed separately.

Underground Mines

Underground mining situations constitute the most complex pyritic systems. Variables include the amount of pyrite and its degree of exposure; the rate at which surfaces are refreshed; the location and flow rate of underground water; the nature and location of points of air entry; and the amount, nature, and influence of collapse on both air and water movement. Further, the presence of neutralizing minerals such as $CaCO_3$, $Ca(HCO_3)_2$, and $Mg(HCO_3)_2$ are influential in changing the characteristics of the effluent drainage. To generalize and simplify the situation without a knowledge and understanding of these many aspects is to invite confusion. The statements that follow represent a listing of pertinent physical factors to be considered in the evaluation of an acid producing mine and the indications and prognoses for remedial measures.

Most underground mining to this date is of the room and pillar type, and up-dip drift mines in bituminous coal regions often produce large quantities of acid drainage. However, the geometry and location of the coal bed may lead to significant drainage from other mine types, such as shaft mines in the anthracite regions. Knowledge of water sources and water movement within the system are of prime importance to the understanding of acid production rates, and in the consideration of remedial methods. A feature of primary significance is the function of a mine as an aquifer drainer. A mine, by virtue of the extensive surface area that is exposed, functions as a stimulator or accelerator of drainage of the overlying formation. Where highly permeable strata immediately overlie the coal, mining activity induces an immediate response in terms of high drainage rates. Where relatively tight (impermeable) over-strata

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*Exposed pyrite may be defined as pyrite to which a continuous oxygen supply is available; e.g., pyrite covered by several inches of water is not exposed pyrite, because of the low diffusivity of oxygen in water.

separate the mined zone and aquifer, the response is delayed until collapse exposes the water-bearing zones to the displaced areas.

The rapid release of water during the normal or seasonal period of high flow and during occasional heavy rainfalls cause abrupt flow changes, and help flush and drain the reactive surfaces of the mine environment. This gives a cycle of (a) low or zero rate of water movement past the pyrite, during which oxidation products accumulate near the site, and (b) a flushing-washing cycle that dissolves the salts and gives an initially highly concentrated drainage solution. This cycle imposes a quality shock on the receiving streams. The resulting periodic acid surge, which normally occurs annually, is often superimposed on a relatively constant "base rate" of acid drainage from mines.[6]

During the low-flow portion of the hydrologic cycle, gas transport with resulting oxidation is at its maximum and product transport at its minimum; during the wet hemicycle, the oxidation is at a minimum and the product transport at its maximum.

Consideration in describing fluid (air and water) transport should be given to the following features:

1. Permeability and porosity

   Significant porosity and permeability are usually found in sandstone. However, all sandstone is not porous, for the interstices may be filled with smaller particles of bulking cement (hydrated iron oxide, clay, gypsum, calcite, or silica).

2. Jointing

   Joints are systematic cracks in the rock that arise from load release, and usually run at an angle to the bedding. Several related sets may be present at any one location. These are the conductors or pervious elements in rocks that would otherwise be impervious, and are not manifest at moderate to great depth. Coal, however, is characterized by very close sets of joints called cleat, and some fractions (vitrain) have a microcleat. Joints are often widened by natural forces (gravity, weathering, mass wasting, and vegetation), especially near the outcrop.

   Bedding plane joints are related to the history of sedimentation and the eventual development of planes of weakness or separation parallel to the bedding. Often these are distinct planes between layers of rock, and virtually all bedded sedimentary rocks reflect this phenomenon. These weaknesses are often revealed in the mining process where blasting may effect separation, or where the creation of the void or mined areas amplifies the inherent weakness of the rock. Porous strata,

joints, and bedding planes (when separated) are the basic passageways for fluids, both air and water. The passageways created by mining are important and may in places obscure (such as in collapse areas) the primary route of fluid travel through rock.

Gas transport can be at a high rate where convection is uninhibited throughout a mining complex. Where openings are closed the air must seek other avenues such as through the permeable zones mentioned above.

Water transport is a gravity phenomenon. Infiltrated precipitation may course its way through pervious rock but its course is basically downward, and the regions of flow will normally not be saturated with water. The flow of ground water below the water table tends to be in a more horizontal direction, and pyrite below the ground water table is effectively sealed off from oxidation. Occasionally artesian conditions occur that cause water levels to rise in some mines. Natural drainage finds its path through the mine as a function of the geologic structure and of gravity, and each mine will have individual characteristics. The percolation of water over internal waste, and over and through pillars to eventually reach the mine courses is controlled by porosity and joints, and the interception of water in the more remote areas of the mine.

Strip Mines

In strip mines, the pyritic materials in the high wall constitute a special case of pyritic materials left in place. Because there is no underground mined volume, oxygen transport to the pyrite is restricted to regions relatively close to the high wall surface. Aside from this restriction, the system characteristics of high walls will be similar to those of underground mines. However, the pollution potential of a stripped area resides primarily in the pyrite incorporated in the spoil pile, since the total exposed surface area of this pyrite will generally be much greater than pyrite exposed to oxidation in the high wall.

Depending on the placement of material in the spoil piles, pyritic materials may be at or near the surface. It is unlikely that materials buried several feet or more beneath the surface can undergo significant oxidation because of the restriction of O_2 diffusion to these depths, and the reaction zone is most probably restricted to the outer layers of the pile. This provides easy access and observation, but also presents a rapidly refreshed surface, unlimited air contact with the pyritic surfaces, and susceptibility to an immediate rapid "flush-out" during periods of precipitation. In the past the most reactive materials have been put at the outermost surfaces of spoil piles. There is an increasing awareness of the problems generated by this practice, and in general efforts are currently being made to reduce pyrite exposure by

the burial of high pyrite content materials deep within the spoil piles. In some areas the strata are sufficiently impregnated with pyrite to defy even these procedures; however, present strip mining practices have brought improvements to both the land surface and to drainage water from the affected areas.

Refuse Piles

Refuse piles are very similar to spoil banks as far as morphology is concerned. The pyrite content is often much higher, however, and the matrix generally contains large proportions of clay minerals of the kaolinite or illite groups. Pyritic materials are distributed throughout the pile, rather than being localized, as in the case of spoil piles. The passage of gas or water through a "tight" refuse pile may be highly restricted. Recent examination of refuse piles of clayey nature[7] showed only a 6- to 14-inch zone to have been altered by weathering; below this zone, the main body of refuse material shows little or no pyrite oxidation. A similar situation occurs in many spoil piles, but where the materials are largely of porous nature, percolation and breathing factors become much more pronounced, resulting in thicker zones of weathering.

It should be noted that even though significant pyrite oxidation is likely to occur only in the surface layers of spoil and refuse piles, water of phenomenally high acidity may accumulate in ground water pools within the piles, because of the leaching of concentrated solutions from the outer surface during periods of precipitation.

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SECTION VI

THE CHEMICAL SYSTEM

E. E. Smith

In this section, the chemistry (i.e., the chemical mechanism and chemical reaction kinetics involved in pyrite oxidation) will be examined. In relation to the conceptual model this section will be concerned with chemical rather than physical processes. The transport of reactants to the reaction site are eliminated as constraints on reaction rate, either by design of the experiment or by definition of the reacting system.

Because the pyrite oxidation reaction is so slow under normal conditions, experimental conditions can be used to isolate different mechanisms and individually evaluate the kinetics involved. Two mechanisms have been studied: (1) O_2 oxidation, or oxidation by adsorbed oxygen, in which case oxygen must be transported to the pyrite surface; and (2) Fe^{+3} oxidation or oxidation by ferric ions, in which case Fe^{+3} ions must be transported to the pyrite surface. The following discussion presents the different methods used to evaluate pyrite oxidation in relation to these mechanisms.

Two basic approaches to the study of pyrite oxidation have been used; i.e., (1) the geochemical approach, and (2) reaction kinetics.

GEOCHEMICAL APPROACH

In this discussion, the geochemical area is broadened to include any study which seeks to interpret the pyrite reaction system by use of chemical thermodynamic principles, or equilibrium relationships. Generally this approach uses equilibrium or thermodynamic data to evaluate reaction mechanisms which are possible under the conditions imposed on or by the system. Garrels and Christ[8] provide the most detailed description of concepts used by the several workers in this area. Sato[9] described the geochemical environment of sulfide ores in terms of E_h and pH. From field measurement and experimental oxidations of iron-containing solutions, the probable ranges of E_h and pH for a weathering environment were determined. The oxidation potential for the weathering environment was reported to depend mostly on the reduction mechanism of oxygen.

In a companion paper, Sato[10] attempted to clarify the oxidation mechanism of pyrite by using experimentally determined single electrode potentials of sulfide minerals. Since the electrode potential is determined by the rate-limiting oxidation-reduction reaction, Sato interpreted his results as indicating that the rate-limiting oxidation process is the oxidation of pyritic sulfur to S^o, leading to the initial release of

ferrous ions and S_2 molecules, which are apparently released simultaneously.

Clark[11] also used the E_h-pH representation to define stability fields for pyrite and the pertinent ionic species involved. He described pyrite oxidation as an electrochemical process involving the "corrosion" of pyrite, and thermodynamic calculations were made to show that ferric ions and oxygen are potential oxidizing agents.

Hem[12,13] and his co-workers made detailed experimental studies of the ferrous/ferric equilibrium in natural waters and inferred that natural waters are sufficiently close to equilibrium to allow calculation of both the concentrations and forms of the dissolved iron species. These studies were not specifically related to mine waters, nor to any water having the low pH typical of acid mine drainage.

From geochemical analyses of mine water, Barnes and Clarke[14] concluded that oxygen need not be a major oxidizing agent in pyrite oxidation. The reduction of water to hydrogen was proposed as a possible substitute. Others have shown, from both experimental[15] and thermodynamic[11] considerations, that the oxidation of pyrite in the absence of oxidizing agents such as oxygen or Fe^{+3} ions cannot be explained.

More recently Barnes and Romberger[16] used E_h-pH diagrams to represent stabilities of minerals and aqueous species in solution at different concentrations of iron, carbon, and sulfur. These diagrams led them to conclude that the leading question in the chemistry of acid mine drainage is how low pH is reached at low E_h. (It should be noted that these authors were basing their conclusions on the nature of effluent water and/or water pooled within the mine, which does not represent the composition of water at the pyrite reaction sites within a mine.)

KINETICS APPROACH

Kinetics of O_2 Oxidation

Earlier reports by Braley,[17] Burke and Downs,[18] and Nelson *et al.*[19] disagreed on the effect of oxygen concentration on rate of pyrite oxidation, indicating that rate varies as a function of oxygen concentration from zero to first power.

Clark[11] found the rate to vary with oxygen to the two-thirds power. The nature of the rate-limiting reaction (in a laboratory environment), and the effect of oxygen concentration, temperature, and of water partial pressure in vapor phase* oxidation, have been reported by

*For purposes of this report a vapor phase environment is defined as one in which the vapor phase is the continuous phase; i.e., the pyrite is not submerged in water and water does not fill the voids in the solid matrix.

Morth and Smith.[20] In these studies, experimental conditions were designed to eliminate diffusional or mass transfer resistances. The rate-limiting mechanism was found to be a surface (chemical) reaction under these conditions.

Oxygen Concentration

Jutte[21] extended the work relating oxidation rate to oxygen and nitrogen partial pressure to pressures exceeding 20 atm. A definite decrease in reaction rate with nitrogen pressure (at constant oxygen partial pressure) was noted.

Using the Hougen and Watson[22] adsorption model, a rate equation was derived[23] which correlated well with experimental data:

$$r = \frac{kO_2}{1 + K_1O_2 + K_2I} \quad ,$$

where

k = reaction rate constant,
O_2 = concentration of dissolved oxygen,
K_1 = adsorption equilibrium constant for oxygen on pyrite,
K_2 = adsorption equilibrium constant for inert material on pyrite, and
I = concentration of inert gas.

Water Concentration

Water was found[20] to be a reaction medium rather than a reactant in the rate-determining reactions in natural environments. Oxidation rate was a function of relative humidity in vapor phase oxidation and the rate at 100 per cent relative humidity was the same as in liquid* (aqueous) phase oxidation at the same partial pressure of oxygen.

pH

Smith, Svanks, and Shumate[23] found that change in pH has little effect on oxidation rate at low pH; i.e., below 3.0. However, as the pH is raised, the oxidation rate increases, slowly at first, increasing to the point where the rate doubles every two pH units above pH of 6.0.

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*A liquid phase environment is defined here as one in which water is the continuous phase, or the pyrite is submerged in water.

Pyrite Characteristics

Birle[24] and Clark[11] determined surface areas of different types of pyrite and reported "sulfur ball" to have approximately ten times the BET surface area as "museum grade" pyrite of the same mesh size.

A more detailed mineralogical study of pyrite was made by Stiles.[25] Pyrite found in coals and associated strata were classified according to the nature and sequence of decomposition. Of the seven classes suggested, those of highest reactivity were composed of pyrite masses containing pyrite crystals up to 5 μm in diameter, agglomerated into spheres 10-30 μm in diameter. The less reactive types had crystals of 0.25 to 2-mm in diameter. Caruccio[28] noted that significant variation in grain size accounts for the different reactivities of pyrite samples he examined.

There is no evidence that trace impurities or features other than those that could be described by texture have a major effect on reactivity. Different cations, such as chromium, nickel, copper, and similar ions that are reported to accelerate oxidation in other systems, were added to the reaction mixture with no significant effect. High concentrations of anions such as phosphates did have an inhibitory effect, but in concentrations below 200 mg/ℓ negligible inhibition was noted. The O_2 oxidation rate is remarkably insensitive to concentrations of substances other than oxygen.

Effect of Temperature

The influence of temperature on rate has been noted by a number of investigators.[18,20,27]. Over the range of temperatures comparable to natural conditions, the rate approximately doubles for each 10°C rise.

Desorption of Oxidation Products

Oxidation rates in both vapor and liquid environments do not appear to be limited by oxidation products.[20] Rates are constant for long periods of time. Visible build-up of oxidation products in vapor-phase oxidations do not influence rate. The desorption of oxidation products by adsorbed water is a continuous and effective mechanism for renewing "reactive sites" on the pyrite surface.

Summary of O_2 Oxidation

Quantitative information is available on the effect of

1. temperature,
2. oxygen concentration,
3. pH,
4. water (concentration) partial pressure,
5. surface area or texture, and
6. concentration of iron, sulfate, and other ions on the kinetics of O_2 oxidation of pyrite.

The rate-determining reaction, in the absence of mass transport limitations, is a heterogeneous surface reaction involving an electron transfer from pyrite to the oxidizing agent adsorbed on the surface. A detailed description of the "reactive site" is not now available, although the adsorption of molecular oxygen is undoubtedly a first step in the direct aerobic oxidation mechanism.

Kinetics of Fe^{+3} Oxidation

Work by Garrels and Thompson,[28] who investigated the oxidation of pyrite by ferric sulfate solutions, showed a dependence of the pyrite oxidation rate on the ferric/ferrous ratio, and suggested that the rate-controlling mechanism is related to adsorption of ferric and ferrous iron on the pyrite surface. They also concluded that the rate of oxidation is chiefly a function of the oxidation-reduction potential (E_h) of solution, and is independent of the total iron concentration. Over the range of E_h that could be examined by Garrels and Thompson their results are valid; however, neither conclusion is basically correct in the light of more recent data.

Singer and Stumm[15] have interpreted kinetic data of the type developed by Garrels[28] by using a model involving the cyclic oxidation of ferrous ions to ferric, reduction of ferric by electron transfer with pyrite, re-oxidation of ferrous by oxygen, etc. Noting that oxidation of ferrous-to-ferric ions is slow compared to reduction of ferric ions by pyrite, Singer and Stumm concluded that the rate-limiting reaction in the oxidation of pyrite is the oxidation of ferrous to ferric ions. Based on this model, they reached the conclusions that (1) ferric iron cannot exist in contact with pyritic agglomerates, and (2) the overall rate of dissolution of pyrite is independent of the surface structure of pyrite.

A more definitive study of Fe^{+3} oxidation kinetics has been reported by Smith, Svanks, and Shumate,[23] and Smith, Svanks, and Halko.[29] Using equipment which enabled them to determine anaerobic oxidation rates at very high ferric/ferrous ratios (greater than 10,000-to-1) at constant EMF, these investigators were able to study the effect of ferric/ferrous ratio and total iron concentration on the rate of pyrite oxidation.

By applying an adsorption model in which ferrous and ferric ions compete for adsorption sites on the pyrite surface, a rate equation

was derived which gave an excellent correlation of the rate data. Although this does not constitute proof, the correlation indicates that an adsorption phenomenon is a likely mechanism in Fe^{+3} pyrite oxidation. If so, the relative adsorption of ferrous and ferric ions, together with the rate of production of ferric ions, will determine the Fe^{+3} oxidation rate.

A large difference was noted in the adsorption on pyrite of ferrous ions relative to ferric, for sulfur ball compared to museum grade pyrite. In each case the adsorption equilibrium constant for ferrous is greater than ferric, but the selective adsorption of ferrous on museum grade pyrite is much greater than that for sulfur ball.

The significance of E_h (or more precisely, EMF for the system studied) was also examined. The data indicated that the oxidation-reduction potential of the solution had, in itself, little effect on oxidation rate. The fundamental variable was the ferric/ferrous rate which, in the system under examination, determined the EMF (the dependent variable). As the EMF was raised to the point where essentially all the iron was in the ferric form, the rate leveled off. In solutions with very little iron less than 3 ppm) the oxidation rate, even at high EMF's, was negligible.

Simultaneous O_2 and Fe^{+3} oxidations were carried out by Smith, Svanks, and Halko.[29] The rates were independent of one another over the range of conditions investigated; i.e., the O_2 oxidation rate was not influenced by the EMF or total iron concentration in the solution. At the same time, the partial pressure of oxygen had no effect on the Fe^{+3} oxidation. It therefore appears that the "reaction sites" for O_2 and Fe^{+3} oxidation of the pyrite are not the same.

Based on these data, the rate-determining regime of pyrite oxidation was described in terms of the dissolved oxygen concentration and of the ferric/ferrous ratio at the reaction site. Comparison of rates shows that in order for the Fe^{+3} rate to be significant in an environment exposed to air with more than 15 per cent oxygen, the ferric/ferrous ratio must be greater than 0.3 (24 per cent ferric). Such a high ferric/ferrous ratio in waters in contact with pyrite below pH 3.0 can only be achieved by microbial activity. At higher pH where the chemical oxidation rate of ferrous ions is much greater, the concentration of ferric ions, because of their limited solubility at higher pH values, is too low to develop a significant Fe^{+3} oxidation rate. These data also contradict the model of Singer and Stumm,[15] since an appreciable concentration of ferric ions can exist, at steady-state conditions, in the presence of pyrite. In addition, oxidation rate is proportional to pyrite surface area in aerobic oxidation.

Summary of Fe^{+3} Oxidation

Quantitative information is available on the effects of ferric/ferrous ratio and total iron concentration on the Fe^{+3} oxidation of pyrite. The following kinetic model, based on the competitive adsorption of ferrous and ferric ions on reactive sites of pyrite, provides a good quantitative expression of oxidation rate as a function of ferric/ferrous ratio and total iron concentration:

$$r = \frac{k\sqrt{Fe^{+2}/Fe^{+3}}}{1/\sqrt{Fe^{+3}} + \sqrt{K_1} + \sqrt{K_2}\sqrt{Fe^{+2}/Fe^{+3}}} \quad ,$$

where

k = reaction rate constant, and
k_1 and k_2 = adsorption equilibrium constants for ferric and ferrous ions.

GEOCHEMICAL VS. KINETICS APPROACH

Thermodynamic or equilibrium relationships between minerals and solutions are not intended to describe the kinetics of a process or set of reactions which may occur as the system is displaced from equilibrium. Application of oxidation-reduction potential (E_h) vs. pH relationships have been very helpful in representing stability fields of minerals and chemical sediments under conditions close to calculated equilibrium conditions in which the quality of the solution phase in contact with the mineral was known. However, the application of these geochemical concepts to acid mine drainage is more limited than normally considered. For defining solubility regimes of solutions such as mine effluents in relation to the mineral environment, these concepts are useful. In this case, reactions involved are fairly rapid, equilibrium conditions are approached, and reactions occur largely within a solution of determinable composition.

However, as a means of describing the extent and rate of pyrite oxidation, the geochemical approach does not appear to be applicable, and in a sense is misleading. Two facts account for this observation: (1) the rate-determining reaction is a surface (not solution) reaction, and (2) the pyritic system is far removed from equilibrium at the reactive sites. As shown by the conceptual model, the major source of acid mine drainage is from pyrite exposed to a vapor phase. Solution concentrations as determined on effluent water or ground water from within or around the mine are therefore not characteristic of the adsorbed water in contact with the reactive pyrite area. There is evidence that oxidation of pyrite is not an electrochemical process in the same sense as is corrosion of metals. Although reactions involving an oxidation-reduction step are, by definition, electrochemical in nature, it appears that the rate of electron transfer (oxidation) is independent of solution E_h;

Fe^{+3} oxidation is determined explicitly by ferric/ferrous ratio and total iron concentration, not E_h.

At this point it appears that the chemical oxidation of pyrite is better interpreted using an adsorption model rather than an electrochemical or thermodynamically defined model. Changes in chemical oxidation rates with oxygen and ferric and ferrous ion concentration can be accurately predicted on the basis of equations derived from the adsorption model.

CHEMICAL ANALOGY OF MICROBIAL SYSTEMS

The bacteria involved in the microbial catalysis of pyrite oxidation have been reported to function through the oxidation of ferrous ions to ferric. Dugan and Lundgren[30] note the energy supply for Ferrobacillus ferrooxidans to be the oxidation of ferrous ions. Large increases in oxidation rate were noted[27,31] when large quantities of bacteria were added to the reaction system.

Silverman[32] suggested that bacteria operate through both a "direct" and "indirect" contact mechanism in oxidizing pyrite. Direct oxidation implies the oxidation of pyrite through direct electron transfer between the cell and pyrite on which the cell is adsorbed. Indirect oxidation occurs by oxidation of pyrite by ferric ions, the ferric ions being generated by bacterial oxidation of ferrous ions in solution.

Bailey[33] followed the rate of pyrite oxidation as a function of ferric ion concentration in a biological system and observed no significant change in rate until the bacteria had oxidized the iron in solution to 70 or 80 per cent ferric. This indicates "indirect" oxidation is of primary importance although it does not rule out a significant contribution by direct oxidation.

Recent unpublished data show that in terms of the ferric/ferrous ratio generated by bacteria, the corresponding oxidation rate is equivalent to that predicted on the basis of non-biological Fe^{+3} oxidation studies; this would indicate the "indirect" oxidation mechanism by microbial action.

If this is true, the Fe^{+3} oxidations described earlier are chemically analogous to the microbiological system. In the laboratory-controlled Fe^{+3} oxidation system, the rate of ferrous-to-ferric oxidation is controlled at any desired level. In microbial systems, a steady-state condition is (or can be) reached in which the rate of pyrite oxidation, as determined by ferric/ferrous ratio and total iron concentration, is equal to the rate of ferrous ion oxidation required to maintain the ferric/ferrous ratio.

SECTION VII

THE BIOLOGICAL SYSTEM

P. R. Dugan and C. I. Randles

In general the involvement of biological systems in acid mine drainage can be arbitrarily divided into three categories:

A. The influence of acid drainage on biological systems.
B. The influence of organisms on formation of acid drainage.
C. Biological means of abatement and treatment.

Although pertinent literature references number several hundred, an attempt has been made to cite only recent monographs, reviews, and reports which are not generally available in the literature.

REQUIREMENTS FOR MICROBIAL GROWTH

Distinction between two categories of microbes is made on the basis of nutritional requirements. Both types have been discussed extensively in the literature.[34-38]

Autotrophic microorganisms are those organisms which utilize carbon dioxide, either oxidation of minerals or photosynthesis as their energy, and a few trace minerals and/or vitamins as additional nutrients. This type of microbe, which includes the Thiobaccillus-Ferrobacillus group of bacteria as well as algae, can therefore grow in a minimal nutritional environment since all of the minimal requirements are readily available in natural water (acid water in the case of Thiobacillus-Ferrobacillus).

Heterotrophic microbes are those which depend upon the oxidation of reduced organic compounds for their energy in addition to their cellular carbon requirements. They also have nutritional mineral and/or vitamin requirements similar to the autotrophic organisms. The heterotrophic microbes include the Desulfovibrio-Desulfotomaculum group of bacteria that have been recommended as possible agents for acid water treatment.[34] In general, specific differences among species of heterotrophic microbes is reflected in differences among types of organic compounds required by each species. This category of organism is somewhat more fastidious nutritionally than the autotrophic category and nutritional requirements vary widely.

It should be pointed out that all organisms do not fall neatly into one category or the other. Many organisms are known which have the facility to adapt either to an autotrophic or heterotrophic mode of existence and are referred to as facultative autotrophs or facultative heterotrophs.

THE INFLUENCE OF ACID DRAINAGE ON BIOLOGICAL SYSTEMS

It is generally recognized that acid drainage has a deleterious influence on multicellular species of plants and animals.[39,40] However, many protist organisms (bacteria, algae, yeasts, and filamentous fungi) have the capacity to live in a mine acid environment. Indeed, certain bacteria (i.e., certain Thiobacillus-Ferrobacillus) are acidophilic and contribute to acid formation via their metabolic activities. A summary report of the activities of microorganisms in acid mine drainage is available.[34]

THE ROLE OF THE THIOBACILLUS-FERROBACILLUS GROUP OF BACTERIA

Reports pertaining to isolation and correlation of the iron and sulfur oxidizing chemoautotrophic bacteria of the Thiobacillus-Ferrobacillus group indicate that their correlation with acidic coal mine discharge is nearly 1; i.e., the bacteria can always be isolated from acidic coal mine drainage. Although positive correlations do not establish a cause and effect relationship, considerable evidence has accumulated which strongly implicates the bacteria as contributive agents in the formation of acid from reduced pyritic materials.[34,35,38,41,42]

The unique feature of acidic mine environments is the proximity of pyrite (FeS_2) or related mineral to the substance being mined. In iron pyrite both the iron and sulfur are in the reduced state (Fe^{+2} and $S^{=}$) and both can be oxidized by bacteria with an ultimate production of acid (H^{+}). The resultant end products are ferric iron (Fe^{+3}), sulfate ($SO_4^{=}$), and acid (H^{+}), all of which characterize acid mine drainage.

MECHANISM OF ACTION OF THE MICROBIOLOGICAL PRODUCTION OF ACID FROM REDUCED IRON AND SULFUR COMPOUNDS

Bacterial oxidation of ferrous iron proceeds in the following generalized manner:

$$Fe^{+2} \rightarrow Fe^{+3} + \text{electron} \quad ,$$

where the liberated electron is used by the bacterium as an energy source and for the ultimate reduction of CO_2 into new cell material.

Ferric iron produced biologically will either react with sulfide nonbiologically,

$$8Fe^{+3} + S^{=} + 4H_2O \rightarrow 8Fe^{+2} + SO_4^{=} + 8H^{+} \quad ,$$

and result in recycling ferric to ferrous iron which is then again available to Ferrobacillus bacteria as an energy source; or ferric iron will react nonbiologically with water,

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad ,$$

to form yellow-brown ferric hydroxide precipitates and acid.

Acid is also produced microbiologically as the result of direct oxidation of reduced sulfur compounds. Several metabolic reactions have been elucidated and these reactions are the subject of an excellent review by Trudinger.[43] In this context it must be recalled that the biological oxidation of sulfide to sulfate involves several intermediary steps, not all of which are completely understood. No single species of organism can be expected to possess all of the enzymes necessary for all known sulfur oxidation pathways. However, the following generalized reactions will serve to illustrate how H^+ and $SO_4^=$ can be produced as the result of metabolism of reduced sulfur compounds by bacteria:

(1) Oxidation of sulfur probably proceeds by reduction of sulfur by glutathione (GSH) to glutathione polysulfide and subsequent oxidation of the GSS_xH

$$S^o + 2GSH \longrightarrow H_2S + GSSG$$

or

$$S_8^o + GSH \longrightarrow GSS_8H \longrightarrow GSS_6H + S_2O_3^= + 2H^+ \qquad (21)$$

(S_8^o: (elemental sulfur); $S_2O_3^=$: (thiosulfate); O_2, H_2O, O_2, H_2O)

$$GSS_4H + S_2O_3^= + 2H^+$$

etc.

in which a net accumulation of thiosulfate and acid could be produced or further used in biological reactions.

(2) Oxidation of thiosulfate ($SSO_3^=$)

$$S_2O_3^= + 2O_2 + H_2O \rightarrow 2SO_4^= + 2H^+ \qquad (22)$$

Thiosulfate produced in reaction (21) is ultimately oxidized biologically to sulfate and acid through several steps. One likely mechanism is via the splitting of thiosulfate into sulfide ($S^=$) and sulfite ($SO_3^=$). Sulfite can be oxidized to sulfate microbiologically in two ways; i.e., (a) via sulfite oxidase enzyme (E) which can be generalized as

$$E + SO_3^= \rightarrow ESO_3^- \xrightarrow{H_2O} E^= + SO_4^= + 2H^+$$

where E represents the enzyme, or (b) the adenosine phosphosulfate (APS) reductase pathway which is somewhat more involved.[37,44]

(3) Sulfide ion can be oxidized biologically via reactions similar to those shown in reaction (21).

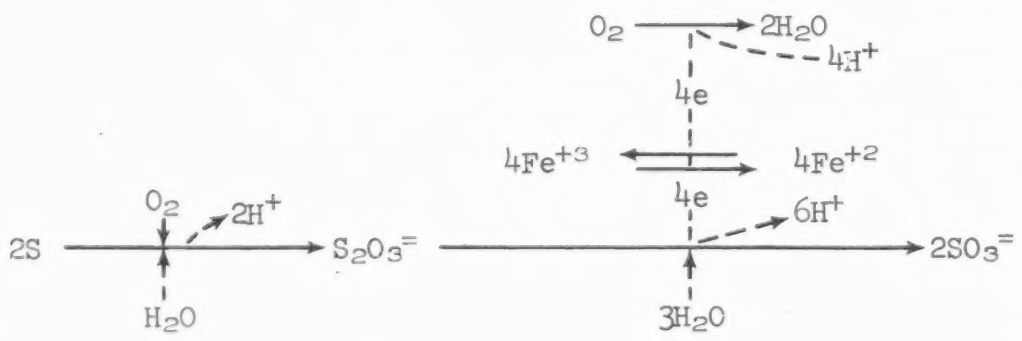
CONSIDERATION OF MECHANISMS OF PYRITE OXIDATION

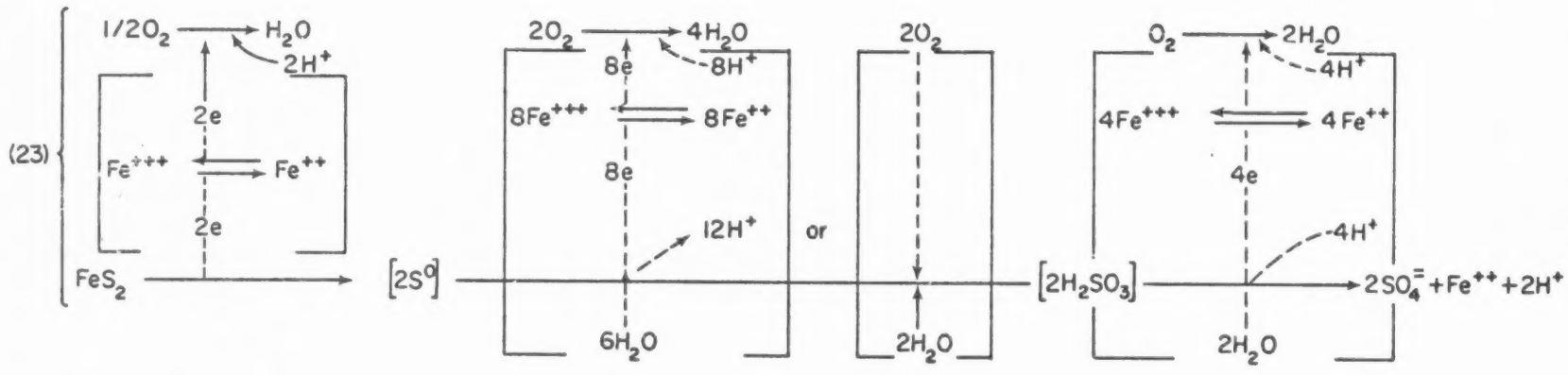
Devising and assessing potential controls of acid formation in various types of mines, refuse piles, and associated materials depends upon an understanding of the processes involved in the oxidation of pyritic materials under the variable conditions existing at the actual sites.

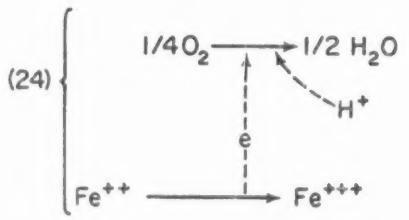
It is appropriate here under "biology" to look at the problem of pyrite oxidation from a somewhat different viewpoint; namely, reaction mechanisms in the oxidation. For purposes of discussion we have set up a minimal reaction scheme (Fig. 7). This has the virtue of allowing us to visualize the process and the factors that might be important in determining the rates of the process. It serves as a guide in directing attention to various important facets of pyrite oxidation which may not be evident from stoichiometric equations or from reaction kinetics.

Some factors are obvious from the stoichiometric equations commonly employed [Eqs. (1)-(3), Section IV] but other factors are not obvious because of catalytic activity or because they are "crossed out" of the reaction equations. It is also valuable to consider possible reaction pathways because the overall reaction kinetics may or may not reveal these mechanisms, and different parts of the reaction may be kinetically important under different conditions.

In regard to Fig. 7, it is not the intention for this diagram to describe the mechanism of pyrite oxidation; it is designed to illustrate the probable minimal complexity of the process and provide a basis for discussion and experimental work. It is possible that the reaction to 2S does not involve, as implied by Eq. (23), a removal of 2e (electrons) from the 2S. The oxidation may involve removal of electrons from iron in the pyrite, the oxidized iron then could pick up electrons from the $2S^{=}$ and be reauced again. This would involve two iron atoms, or one iron atom going through two cycles. It is also possible that the reaction from 2S to $2SO_3^{=}$ takes place in two steps, with the utilization of an oxygen molecule in each, and that these may differ mechanistically; e.g.,







(25) $Fe^{+++} + 3H_2O \longrightarrow \underline{Fe(OH)_3} + 3H^+$

Fig. 7. Possible Scheme for Mechanisms of Pyrite Oxidation

This would provide an explanation for thiosulfate observed during alkaline oxidation of pyrite, the iron for the second stage being tied up and not available for effective catalysis or electron transfer. It is also possible that this reaction is facilitated by the alkaline environment, or iron tie-up, so that the normal reaction is switched to this side reaction.

It is necessary to accept the stoichiometric equations describing pyrite oxidation because these provide the necessary base for examining the mechanisms and kinetics of the acid-forming process, and define certain irreducible minima which must be considered.

There seems little doubt that the problem of acid formation involves the oxidation of pyrite in two separable oxidative steps [Eqs. (1) and (2)] followed by a nonoxidative formation of ferric iron precipitate, depicted in Eq. (3), as ferric hydroxide. These equations suffice for stoichiometric and thermodynamic purposes, but do not necessarily serve kinetic or reaction mechanism purposes, beyond supplying the bones upon which the body of kinetics and mechanisms is built.

Participants in the reaction determine the kinetics of those reactions that are thermodynamically possible. Some of the participants are obvious from the stoichiometrics of the reaction. Others are not obvious because they serve catalytic functions or "cancel out" in the overall reaction. Both kinds of participants, which are not basically different since they both indeed participate in the reaction, may influence the kinetics of the reaction. It is with the second type of participants that knowledge of reaction mechanisms is particularly pertinent and, conversely, where kinetic information can be relevant to determining reaction mechanism.

As an example, if we look at Eq. (1), it is not apparent that ferrous iron has anything to do with the reaction since the ferrous iron of pyrite is not apparently oxidized. From a kinetic, or mechanistic point of view, however, there is growing evidence that the rate-limiting step in pyrite oxidation may indeed be this oxidation of ferrous to ferric iron. This fact is obscured by the rapid reduction of the ferric iron back to the ferrous state again.

In these reactions it is relevant to note that the pyrite contains two oxidizable constituents, the iron and the sulfur, and that 93.5 per cent (14/15) of the oxygen consumed in the overall reaction is employed in the oxidation of the sulfur component and only 6.5 per cent in the iron component, while none of the oxygen consumed in Eq. (1), stoichiometrically speaking, is used in iron oxidation.

If iron were, kinetically or mechanistically speaking, the consumer of oxygen in Eq. (1), it being then reduced to ferrous iron, it would have to be oxidized and reduced 14 times during the oxidation of the sulfide portion. This is the extreme. To the extent that oxygen

might directly participate in oxidation of the sulfide portion, either by direct oxygenation or by serving as a direct electron acceptor, the number of times the iron portion would be oxidized or reduced would be lessened.

To put it another way, seven pairs of electrons must be transferred from the sulfur portion of the molecule to oxygen (2 per oxygen atom, 4 per oxygen molecule). The ferrous iron is capable of transferring only one electron at a time. If it is the only mediator between the oxidation of the sulfur in pyrite and the reduction of oxygen, 14 molecules of ferrous iron would have to be oxidized and 14 of ferric iron reduced for each pyrite molecule oxidized to the ferrous and sulfate levels.

A minimum of two turnovers would be necessary because the maximum amount of oxygen that could be used directly by oxygenation would be $3O_2$. It is unlikely that oxidation from the sulfite to sulfate levels involves oxygenation, or even direct electron transfer to oxygen, so that four more electron transfers through ions are likely here. If so, this would limit direct oxygenation (direct electron transfer to oxygen) to the involvement of $2O_2$. In this case, six turnovers of ferrous-ferric ion would be necessary.

To illustrate this, let us break down the oxidation of the other portion of the molecule into three hypothetical but possible steps.

$$(S_2) = \rightarrow 2S^o + 2e \qquad (26)$$

$$[2H^+ + 2e + 1/2O_2 \rightarrow H_2O]$$

$$2S^o + 2O_2 \rightarrow 2SO_2 \qquad (27)$$

$$SO_2 + H_2O \rightarrow SO_3^= + 2H^+$$

$$2SO_3^= + 2H_2O \rightarrow 2SO_4^= + 4H^+ + 4e \qquad (28)$$

$$4H^+ + 4e + O_2 \rightarrow 2H_2O$$

Reaction (26) involves going from the oxidation level of the sulfur in pyrite to the level of sulfur itself, which, by its nature, would necessarily somehow involve electron transfer.

Reaction (27) as depicted would be the only step in which direct action of oxygen would be possible, although this is admittedly hypothetical. It could conceivably be an oxygenation, the only probable place where this could occur, or it could also involve electron transfer either directly to iron or through iron.

Reaction (28), as indicated above, undoubtedly does not involve direct oxygenation and probably not direct electron transfer to oxygen.

These reactions have been selected for illustration of what are probably the minimal steps, mechanistically, that can be visualized in oxidation of the sulfur component of pyrite, and the most direct pathway. This is relevant kinetically since it indicates minimal relations of participants in the reaction. For example:

(1) This would suggest that rates of oxidation of Fe^{+2} would need be 2, 6, or 14 times the rates of oxidation of pyrite, assuming this oxidation is rate limiting and that ferric iron acts as oxidant of the sulfur portion of pyrite in these different ways.

(2) If reaction (27) is necessary to the oxidation of the sulfur portion of pyrite, oxidation beyond the level of elemental sulfur could not occur anaerobically (e.g., with Fe^{+3} as oxidant). Since ferric iron can apparently suffice, in the absence of oxygen, to bring about the oxidation of sulfide sulfur to sulfate, it indicates that oxygenation is not an obligatory step in the oxidation and that all the oxygen found in the sulfate can come from water.

Reaction (23) in Figure 7 [Eq. (1)] is highly exergonic, essentially irreversible, and hence there are no thermodynamic barriers to its occurrence. Further, it is unlikely that changing concentrations of products can significantly affect the reversibility of this equilibrium reaction with attendant rate effects. That the product may in some other way influence rate is not excluded (e.g., $SO_4^{=}$, H^{+}, Fe^{+2}).

Concentrations of reactants, however, must be carefully considered. First, it is obvious that this reaction cannot possibly proceed as written unless at least all three reactants are present, and that the influence of at least these three reactants must be considered.

(a) FeS_2. The insolubility of this reactant almost perforce means that we must consider an effective concentration which would be much less than the total concentration present. There does not seem to be any actual measure of this effective concentration, but certainly surface area would be a closer approximation of effective concentration than total concentration, and might be the relevant measure.

(b) Oxygen concentration will be a factor in establishing the reaction rate, providing one or both of the other two reactants are not limiting. Unless some other oxidizing agent is employed (e.g., Fe^{+3}), there is no alternative.

When we consider that 3.5 molecules of oxygen are consumed in reaction (1), with the concommitant change of pyritic sulfur from a -1 to a + 6 oxidation state, it is necessary that the reaction be more complex than written in Eq. (1).

(c) H_2O. The presence of water as a reactant in the equation should forestall any comments that it is not a reactant; it may also be significant as a reaction medium but this would be an additional function. Not showing up in the stoichiometry of the reaction is the fact that wherever iron is the intermediary in electron transfer between pyrite oxidation and oxygen, water must be the source of the oxygen that ends up in the sulfate. Hence, it is most probable that water is more important than indicated by the stoichiometry of the reaction.

All three of these materials have, within limits, been shown to be determining factors in discussing either the kinetics or the mechanism of pyrite oxidation.

Reaction (24) of Figure 7 [Eq. (2)] is not a highly exergonic reaction; hence, it is readily reversible. This places this reaction in a different light than the other two since it allows the reversible oxidation and reduction of iron under the conditions of pyrite oxidation and hence has catalytic potentialities both chemically and biologically. This is not brought out in the stoichiometry of acid formation because the ferric iron measured (or ferrous iron disappearing) is that which enters reaction (25). Stoichiometrically, reaction (23) may be the only truly pertinent reaction in acid formation, but kinetically reaction (24) may be most important.

Reaction (25) [Eq. (3)], the hydrolysis of Fe^{+3}, yields the end product of pyritic iron oxidation and in most circumstances ferric precipitates do not form at the site of pyrite oxidation, indicating that the ferric iron that may be formed by reaction (24) at the oxidation site is rapidly reduced again rather than hydrolyzed. Thus, reaction (25) can be considered a secondary process not directly involved in acid formation <u>per se</u>.

There seems little doubt that iron oxidation is a significant factor in pyrite oxidation; this may be through reaction (23) involving oxidation of the iron in pyrite, which does not show up in the stoichiometric equation, or it may be through iron in solution, as in reaction (24), or both. Distinguishing between these two possibilities is important.

In view of the admitted slow rate of the chemical oxidation of ferrous iron by oxygen in acidic solution, and the role of this oxidation in pyrite oxidation, the role of bacteria catalyzing ferrous iron oxidation in accelerating pyrite oxidation is readily seen.

The extent to which the ferric-ferrous couple participates in pyrite oxidation via an electron-transferring function will be pertinent to the extent of involvement of iron-oxidizing bacteria in determining rates of oxidation. Minimally, two moles of ferrous iron would need to be oxidized per mole of pyrite oxidized, and, maximally, fourteen moles would need be oxidized. From our present imcomplete knowledge, it would seem that at least six moles would be needed.

BIOLOGICAL MEANS OF TREATMENT AND ABATEMENT

Treatment

A report on the potential use of heterotrophic anaerobic bacteria (Desulfovibrio and Desulfotomaculum) as a means of reducing sulfate tc sulfide in acid mine water has been published.[34,44] This process has several advantageous aspects.

(a) Sulfide will reduce ferric ions to ferrous ions and will precipitate ferrous ions as insoluble FeS, thereby removing virtually all iron from solution.

(b) It has also been reported that precipitated FeS is amenable to mechanical separation which would yield a sludge that could be further processed to yield a sulfide reagent for further use in treating mine water.[45]

(c) Metabolism of the heterotrophic Desulfovibrio-Desulfotomaculum group of bacteria also results in a net increase of pH of their environment.

(d) Metabolic byproducts of the anaerobic bacteria have an inhibitory effect on the chemoautotrophic iron-oxidizing bacteria.

Two primary difficulties must be overcome to accomplish sulfate reduction in acidic waters. Dissimilatory sulfate-reducing bacteria require an oxidation-reduction potential of -150 to -200 mV; therefore the water must be made anaerobic. Secondly, a source of organic nutrients to supply energy and carbon for the heterotrophic anaerobes is required. The addition of organic materials is favorable to the establishment of anaerobic heterotrophic microflora in acidic water.

The process of biological sulfate reduction can be manipulated in the laboratory to increase the overall efficiency, and attempts to scale up the process seem to be successful. This suggests that such a process could be developed into a practical abatement method at specific locations. Potential methods for accomplishing this process are lagooning, design of a facility similar to those used for anaerobic sewage digestion, and conversion of certain mines into anaerobic mines where the reduction process would proceed directly in the mine.

The carbonaceous energy source for sulfate reducers could be wood (saw) dust, sewage, waste paper or other domestic waste, algae, aquatic weeds, or other waste vegetable material. Activity of a third group of bacteria was essential to accomplish this process. The third group, referred to as cellulose digesters, also proliferates under acidic conditions and any low-cost cellulose should be able to supply nutrients to the sulfate reducers. The process of microbiological cellulose digestion is exothermic and results in substantial heat liberation which could be advantageous in treatment of water in cold climates.

Pretreatment

Processes involving the use of lime or carbonate treatment to precipitate ferric iron or $Fe(OH)_3$ from solution are quite sensitive to pH. A high degree of iron removal at near neutral pH values depends upon a high ratio of ferric to ferrous ion. Autotrophic bacteria (Thiobaccillus-Ferrobacillus) have been used successfully in the laboratory to convert ferrous to ferric ion as a prelude to precipitation with limestone.[42] High-rate microbially catalyzed oxidation of ferrous iron can be carried out at pH values of 2.5 to 3, while the chemical oxidation of ferrous iron by oxygen is extremely slow at the lower pH values. Microbial oxidation of iron to the ferric form at low pH, followed by neutralization of the waste to precipitate the iron offers the possibility of higher oxidation rates, closer pH control, and better process efficiency than when oxidation and neutralization must be carried out simultaneously. It is anticipated that commercial use of the microbial conversion will require a heat input to raise mine water to optimum temperature for the biological iron oxidation (20-25°C). Success of this method of treatment will depend upon availability of lagoon area, concentration of iron in solution, and total cost of treatment including the lime precipitation-neutralization and precipitate removal steps.

Abatement

As stated at the beginning of this section and elsewhere[34] it is possible to inhibit metabolism of the autotrophic iron and sulfur oxidizing bacteria in the laboratory with the use of chemicals which are quite innocuous to most other living organisms; e.g., alpha keto acids and carboxylic acids. Preventive methods which utilize antimicrobial agents should prove successful at specific locations; that is, success in the prevention of this type of pollution would depend upon the ability to inhibit causative bacterial metabolism at the origin. The location and inhibition of microbial activity should not be problematical in the case of refuse piles but may be quite difficult in the case of abandoned drift mines.

The type of antimicrobial agent to be employed in a field situation is a matter that must be further explored. Some fruitful investigations with regard to inhibition of iron and sulfur oxidation by

autotrophic bacteria have been carried out; however, preliminary evidence suggests that chemical inhibitors might be more practical with reference to cost, availability, ease of application, and lack of toxicity for organisms other than the iron and sulfur oxidizers. Further work in this direction is needed.

An additional approach relating to pyrite oxidation abatement via biological means is the use of bacteriophage to eliminate bacterial catalysis. Reports by Shearer and Everson[46] and Shearer et al.[47] gave serious consideration to this possibility.

Three aspects should be considered with regard to phage inhibition of the acidophilic autotrophic bacteria:

1. Convincing evidence for establishing the presence of phage particles which are virulent for acidophilic Thiobacillus or Ferrobacillus has yet to be prepared.

2. In relationship to our general knowledge of bacteriophage, known types of phage are highly specific to host strains within a single species and host species become modified through genetic and selective processes to a point where they may not be susceptible to a lytic phage. This suggests that use of phage to lyse a spectrum of Thiobacillus-Ferrobacillus strains of bacteria in the field would not be practical if they were available. The situation would be somewhat analogous to the unsuccessful attempts to cure enteric bacterial diseases by placing enterophage in the tract.

3. Finally, bacteriophages feature protein type shells and are very sensitive to pH and ionic strength; it is not likely that specific proteins can remain functional over the pH and ionic strength range encountered in mine acids.

The most recent report of Shearer and Everson[48] indicates that they now believe Caulobacter species to be responsible for Thiobacillus-Ferrobacillus inhibition in their experiments, and that the inhibition is due to the production of specific antibacterial agents by Caulobacter. It should be noted that most data related to inhibition of acidophilic autotrophs can be interpreted as the activity of chemical antimicrobial agents. Disputes with regard to data interpretation do not discredit sound experimental data and the experimental observations may be quite significant. However, data interpretation is strongly dependent on experimental design, and extreme caution is required in this context if such lines of investigation are to be fruitful.

Regardless of the mechanism of biologically-produced agents inhibitory to Thiobacillus-Ferrobacillus species, the utility of such approaches will depend upon the ability to get the agent in contact with the bacteria in the field. Evidence for the site of pyrite oxidation presented in other sections of this report and in the general literature suggest that this may be very difficult in underground mines but may be a promising approach in refuse piles.

CRITICAL SUMMARY

The biological research effort related to the acid mine problem is minimal by comparison to efforts directed toward chemical neutralization. There appears to be an overwhelming amount of evidence accumulating in the literature which establishes that (a) pyrite is oxidized at significant rates by the acidophilic autotrophic bacteria; (b) these bacteria are always found in acidic mine drainage; (c) the only known sources of energy for the bacteria in the mine water environment is the oxidation of Fe^{+2}, $S^{=}$, or pyritic material; (d) the presence of the bacteria in the water therefore indicates that a finite amount of reduced iron or sulfur already had been oxidized to produce the cells observed; and (e) in a continuous flow situation where approximately 10^{8} cells per ml are continuously being removed, a finite amount of pyritic material is continuously being oxidized by the bacteria.

A gross calculation based upon experimental data indicates that 0.16 mole of iron oxidized yields approximately 10^{11} cells, or 0.64 gram moles of iron oxidized will yield the number of cells found in a gallon of water. If the flow of water away from the source is 100 gal/min then 64 moles of iron would have been oxidized per minute to yield the cells being lost. The efficiency of energy conversion has been reported to be 10 to 30 per cent; therefore, $64 \times 3 = 192$ gram moles of iron would be the minimum Fe^{+2} oxidized per minute in the above example; 192 moles of Fe^{+2} is the amount found in about 50 lb of pyrite. These calculations are only intended as illustrations and no accounting has been made for energy released from the sulfide in pyrite, which is about 10 × greater per mole than that from Fe^{+2} iron. Assuming that all ferrous and sulfide in pyrite were oxidized to ferric and sulfate it would have required oxidation of 5 to 50 lb pyrite per minute to yield the acidophilic autotrophs in a stream having a flow of 100 gal/min.

If the above assessment is reasonable, then the basic question to be resolved in this regard is "What is the relative significance of microbial pyrite oxidation in comparison to chemical or nonbiological oxidation in a variety of field situations?"

If it is concluded that biological oxidation is significant in proportion to nonbiological oxidation, then efforts must be expanded to determine the most effective means of inhibiting the oxidations. One promising means is via specific anti-microbial chemicals, providing the compounds can be placed in proximity to the target organisms in the field and are relatively specific for the target. Further efforts should be undertaken to study the basic metabolism of the organisms in order to understand what inhibitions are effective, how to use them, and under what circumstances they would be most effective.

In situations where acid formation cannot be prevented, more efficient methods of treatment which appear promising in specific situations are (a) reduction of sulfate to sulfide via anaerobic bacteria--a process which has several "spin-off" advantages that might be favorably

compared to chemical neutralization processes, and (b) adsorption of metal ions by biologically produced polyelectrolytes which can then be removed by conventional waste treatment technology.

Effects of acid mine drainage on the biological systems in nonpolluted receiving waters should be more carefully evaluated in order to determine the extent of treatment and abatement that is necessary. This should include an assessment of all components of the acid mine drainage.

SECTION VIII

AT-SOURCE ABATEMENT - PRACTICAL CONSIDERATIONS

R. A. Brant and K. S. Shumate

Throughout this report, the writers have attempted to emphasize the importance of viewing acid mine drainage production as a dynamic reaction system. In controlling such systems, all pertinent mass transports, reactions, and reaction kinetics must be accounted for, and any successful abatement procedure must exert positive control on the rate of some step in the overall sequence of mass transports and reactions. Specific steps which may be subject to practical control are listed below.

Mass Transport Controls

a. Control of water available to participate in the reaction at the pyrite surface.

b. Control of oxygen available for pyrite oxidation.

c. Control of the rate at which acid products are flushed away from the pyrite surface.

Reaction Kinetics Controls

a. Control of the rate of the oxidation of pyrite by oxygen, by the application of an inhibitor or passivating agent to the pyrite surface.

b. Control of the rate of a microbially catalyzed reaction by the application of agents inhibitory or bactericidal to the bacteria involved in the catalysis.

The two major types of acid drainage sources are underground mines and relocated pyritic materials; the latter category includes refuse piles and strip mine spoil banks. Because the characteristics of the two types of systems are greatly different, at-source abatement procedures will be discussed separately for each case.

UNDERGROUND MINES

Mass Transport Control

Water Availability at the Pyrite Surface

It has been demonstrated[20] that with a relative humidity of 100 per cent, water availability does not exert a rate-limiting effect on the oxidation of pyrite by oxygen. Thus, in any environment wet

enough to provide a continuous occurrence of moisture in the vicinity of pyritic material, there is little hope of limiting water availability at the oxidation site. For example, in the Appalachian coal fields, the relative humidity in underground workings is sufficiently high that the chemical oxidation of pyrite by oxygen is not limited by water availability. Generally speaking, if there is sufficient water to produce mine drainage, there will be sufficient water for the pyrite oxidation reaction. Water diversion is a separate consideration dealing primarily with oxidation product transport, and will be discussed in a later section.

Oxygen Available for Pyrite Oxidation

Past and current attempts to control pyrite oxidation in underground mines have revolved mainly around the control of oxygen access to the exposed pyrite, and virtually all schemes have employed mine seals of one type or another. Fundamentally, mine sealing projects aimed at oxygen transport control can be divided into two categories: (a) control of the rate of oxygen entry to the mine void, which in turn will control mine atmosphere composition; and (b) establishment of an aqueous diffusion barrier, as in the partial or complete flooding of a mine. Both of these abatement mechanisms will be operative to some degree in any sealed mine. Any type of seal across a mine opening will prevent convective transport through that opening and will suppress thermal convection currents within the mine. On the other hand, an air-tight seal will force 'breathing' through the overburden, as discussed in Section V. If a seal causes partial flooding, some exposed pyritic material may be submerged and effectively isolated from the mine atmosphere, and at the same time, the 'breathing' volume is reduced. The relative intensity of these various effects will vary widely from one situation to another. Oxygen entry control and mine flooding will be discussed separately below.

Oxygen Entry Control. The sealing of a mine to prevent all oxygen entry is simple in concept, but difficult to attain. If oxygen entry were eliminated, the oxygen in the mine atmosphere would eventually drop to zero because of gradual consumption of the oxygen present. If the mine atmosphere of a sealed mine levels off at some finite oxygen concentration, it is positive proof that the mine is still providing for oxygen transport into the mine at a rate sufficiently high to maintain an appreciable rate of pyrite oxidation. This appears to generally be the case where mines have been sealed and the atmosphere periodically sampled.[49,51]

The types of seals which have been tried fall into the categories of air seals, meant to stop passage of air, and bulkhead seals, meant both to hold water within the mine and to stop air passage. Air seals may be wet, in which case they pass water through a trap arrangement, or they may be dry, with no provision for the passage of water. There is a long record of both wet and dry air seals used separately or in

conjunction, and recent literature contains many descriptions of such efforts. However, whether or not they are particularly effective in bringing about significant reductions in acid production rates is questionable. Several air (wet) seal and bulkhead developments are currently being given close scrutiny. The U. S. Bureau of Mines has constructed a series of seals in a mine near Pittsburgh, and published reports describe the project and its effectiveness.[49,52] Similarly, a project near Elkins, W. Va.,[53] has generated information. Projects such as these are yielding valuable and urgently needed information. It must be stressed, however, that the interpretation of field data is a difficult and uncertain task, and in the case of underground mines it is necessary to collect pre-sealing base line data for a period of at least one year and preferably for several years. In the opinion of the authors, post-sealing data must be followed for at least five years before a reasonably firm evaluation can be made. The primary reason for this is the wide variation in ground water flow patterns from year to year and the slow response of underground flow systems in regard to the transport of products of pyrite oxidation. Based on 28 months of presealing data and 32 months of post sealing data, Moebs[49] found that the effluent acid load was reduced about 50 per cent in the subject mine.

There are also data interpretation problems other than those associated with hydrologic variability. For example, with regard to wet air seals, the data of Moebs[52] shows a drop in effluent acidity occurring almost simultaneously with the completion of the seals. While this might be equated with a drop in pyrite oxidation, other considerations may account, at least in part, for this phenomenon. In the construction of some wet air seals, a pool of water several feet deep is created. Such a pool may act as a stilling basin in which high masses of solute-rich water will seek the bottom part of the pool. Certain of the flow streams which drain regions of pyrite oxidation will contain extremely high concentrations of oxidation products when they seep into the pool. On the other hand, much of the water entering mines through the exposed roof may contain very little solute, particularly if the roof shale has been drawn or is absent.

The probable points of entry of highly acid water to the mine void are related to the location of pyritic materials in the coal and associated strata, and merit some discussion. When one thinks of a mine with a sandstone roof, the term "acid sandstone" comes to mind. This term is widely used, and is usually confused with pyritic sandstone which contains pyrite that will rapidly oxidize and produce acid products. The term should be abandoned, because it is a misleading generality, and in most cases such materials do not contribute significantly to acid mine drainage.

In moist mines with sandstone roofs, the water entering the mine void directly through the sandstone contains little acid. That which percolates through pyrite-bearing materials (e.g., coal in place, shale, refuse, and exposed pyrite on the floor) picks up high concentrations of acidity. Because of specific gravity differences, the roof

drainage may tend to stratify above the strongly acid drainage in the pool caused by the seal. When the pool fills, the lighter, less acidic water may pour over the lip of the interior baffle wall and emerge at the outby baffle as a relatively good quality water. The conclusion (though possibly erroneous) is immediately available that a dramatic change has taken place in the production of pyrite oxidation products. In time, dynamic equilibrium will be reached in the pool, and the acid will tend to leave the pool as rapidly as it enters. Since the streams of highly acidified water may flow at very low rates relative to the total drainage rate, the time to reach this equilibrium may be considerable, and the true effect of the seal on acid production may not be observed in the effluent drainage for an extended period of time. The time required will depend largely on the relative flow rates of the acid and fresh water streams within the mine. It is necessary to sample the pooled water within the mine at various depths and locations to determine to what degree this phenomenon is occurring.

A third problem in the evaluation of data from sealed mines revolves around the significance of gas composition in the sealed mine atmosphere, and the tendency of sealed mines to breathe under atmospheric pressure fluctuations, as discussed in Section V of this report. Sealed mines have demonstrated mine atmosphere O_2 compositions of from 20 per cent down to 10 per cent or a little less at the point of sampling, which is usually near a seal.[49,51] Also, even in mines which have been sealed as carefully as possible, there have been no documented cases of significant pressure differentials between the mine and the outside atmosphere, indicating that the mines are breathing efficiently with atmospheric pressure variations. This convective breathing is the only means of significant oxygen transport into the mine. As pointed out in Section V, if the equilibrium oxygen concentration in the mine is greater than zero, then the gross oxygen intake is greater than the oxygen utilization within the mine. The net oxygen intake (the sum of oxygen intake and exhaust under pressure fluctuations) will equal the total O_2 utilization within the mine, which will in turn be approximately equal to the sum of oxygen used for carbonaceous material conversion to carbon dioxide, and of oxygen utilization in pyrite oxidation. A knowledge of mine atmosphere volume, atmospheric pressure variation, and mine atmosphere composition (O_2 and CO_2, including variations from point to point within the mine) would allow a rough calculation of pyrite oxidation rate. Such data are scarce, however, the most complete set having been published and discussed by Moebs.[49] It is strongly urged that such data be collected, as a second means of evaluating seal effectiveness.

At this time, it should be concluded that breathing through the enclosing rocks is the basic failure and limiting constraint in air-sealed mines. If a sealed mine is breathing, the locations of the points of air entry may be of considerable significance. It is not likely that the overburden enclosing sealed above-drainage mines would ever be sufficiently homogeneous with regard to air permeability and sufficiently uniform in depth to allow uniform breathing over the entire overburden

area. Rather, the regions of air entry will be at locations where the overburden is either fractured or thin. Whether or not the soil overlying regions of air entry is heavily vegetated may be of significance. Bare porous rock, such as may be present near the mine outcrop, offers little capacity for consuming oxygen as air is pulled in and out through breathing action, and air entering the mine will be essentially at 20 per cent oxygen. If, on the other hand, the air must pass through an accumulation of organic matter at the surface, such as a layer of heavy vegetation, oxygen will be utilized through aerobic biological action in this layer. The oxygen-consuming ability of soil layers high in organic material is reflected in the observation that oxygen is often absent in vadose or phreatic waters, and the deeper soil atmospheres are generally lacking in oxygen because of the demands on the entering atmosphere for its oxygen content.[54] The effectiveness of vegetative or organic layers as an oxygen filter will depend on the relative rates of oxygen utilization in the oxygen-consuming layers and the rate of air transport through the layers by mine breathing. The rate of air influx is dependent on the mine void volume and the rate and amplitude of atmospheric pressure fluctuations, as described in Section V. If the areal extent of the regions through which air is being drawn is also known, then a calculation could be made of the oxygen consumption rate of the soil which would be required for the prevention of oxygen entry. The practical aspects of such an approach have not been investigated, although it is likely that data are available from agricultural studies on the oxygen consumption rates in soil under various conditions. With regard to the problem of finding the breathing vents of sealed mines, the results of a recently conducted effort are presented by Moebs.[49] In the absence of definitive information, the filling in of subsidence holes, with revegetation of the fill or mulch covering, may effectively return such sites to a precollapse condition with respect to O_2 transport. Whether the effect of such an action will be significant depends on the individual situation.

The possibility of applying sewage sludges or other oxygen-demanding materials to breathing areas might be considered. At this time, information on the oxygen consumption kinetics, air permeability, durability, and effective useful life of such materials is not available. It must be remembered that the design life of any at-source abatement procedure, such as mine drainage treatment, must be interminable, and in the long run, operation or maintenance costs will far outweigh initial placement or construction costs.

If the vegetative layer of the confining overburden of a given mine is an effective oxygen filter, then the point of placement of the seals becomes important. Many old seals were placed very close to the outcrop, thus allowing the possibility of breathing through bare rock, as well as placing them in a position of greatest instability and open attack by mass wasting and weathering effects. Some newer approaches place the seal more remotely and thus in a more stable position. Several current projects may respond favorably to the new, more substantial approaches, both by reducing breathing through bare rock, and by assuring integrity of the seal. In any case, selection of the seal site should

be based on a detailed knowledge of enclosing rocks, the seal should be designed against immediate and potential instability, and an evaluation should be made of the route through which oxygen will enter the mine through breathing. With regard to the management of active mines and the planning of new mines, due consideration should be given to the possibility of effectively air-sealing sections of a mine before abandonment of the complex. The following types of air seals have been used in the past, and each should be effective as a closure if the integrity of the seal is maintained:

Type		
I	Native rock, clay pipe and mortar	← (Wet seals)
II	Brick or block, clay pipe and mortar	
III	Block and use of overflow dams to provide water trap	
IV	All of the above without trap drains	
V	All of the above plus backfilling and compaction of immediate outby area	← (Dry seals)
VI	Clay pack	
VII	Other: grout packing of dry openings containing collapse	

Recent advances in sealing techniques may or may not be significant in approaching a solution to the problem. Diversion of water by the use of fill in subsidence areas may fulfill a conceptual need, but the significance of this practice in modifying the total water budget and in reducing air breathing has not been demonstrated in the field. The use of a sealant (e.g., polyurethane foam) around an air seal is probably significant, especially in connection with porous or jointed rocks that can readily conduct air around the seal. The concept of sealing not only the opening but the associated enclosing rocks is certainly an advance, as is the design of a sump pool of large size. With regard to air seals in general, such questions arise as: Will these "curtains" have a reasonable longevity? Will these relatively fragile structures hold against stresses transmitted through the rock? It must be stressed that any mine seal will require regular maintenance and inspection.

The most important question which should be asked, however, is in regard to the concept of air sealing. Is air sealing without the elimination of atmospheric pressure induced breathing fundamentally valid? It is not feasible to make a statement except to point out that past experience with air seals has not demonstrated great success, and present efforts may lend themselves to premature conclusions unless extreme care

is exercised in the collection and analysis of pre- and post-sealing data.

To summarize the discussion on air sealing, it must be emphasized that sealing an opening and sealing a mine against oxygen entry are quite different. Leitch[55] stated 40 years ago that "sealing must be air tight." More specifically, the sealing technique must prevent oxygen entry, whether the mine is actually air-tight or not. If little or no oxygen gains access to exposed pyrite, then acid production will be stopped. However, it must be concluded that air-sealing techniques which have been applied to above-drainage mines do not prevent oxygen entry. There is no reason to assume that in the general case air sealing will decrease acid formation to the degree that subsequent drainage treatment can be avoided. It is even conceivable that air sealing could aggravate acid production in certain instances. For example, consider a situation in which significant concentrations of pyrite are present in shale at or near the top of the coal seam. If the overburden is thin and fractured in places, and if the shale layers are relatively permeable to gas flow, then the shale may act as a conductor of air flow between the coal face in the mine and the fractures in the overburden. Before sealing, atmospheric pressure changes would have resulted in breathing in and out of the mine entries and ventilation shafts, this being the path of least resistance to convective transport. Oxygen transport to pyrite in the shale layers would be largely limited to molecular diffusion. After sealing, atmospheric pressure-induced breathing will again follow the paths of least resistance, which may now be along the shale layers connecting the mine with overburden fractures. Thus, pyrite in these layers would be subjected to the convective transport of air back and forth between the overburden fracture vents and the mine, and oxygen concentrations in the shale could be much higher than prior to sealing, leading to a higher pyrite oxidation rate.

It must be stated that currently available data do not allow a sound interpretation of the results of air sealing, particularly in terms of sealing effects on fundamental mass transport and reaction rates. In the absence of data to the contrary, the authors feel that, in general, air sealing as currently practiced cannot curtail acid production to the degree necessary to make the procedure economically feasible.

A modified air sealing procedure which would counteract the breathing action of a mine may hold promise as a future development. There has been preliminary work on inert gas blanketing of mines,[51,56] but no large-scale demonstration has been completed. If inert gas is introduced into a mine so that a slight positive pressure is always maintained there will be no oxygen entry, and pyrite oxidation will cease. Depending on the size of the mine and the permeability of the overburden, this may require unrealistically large quantities of gas. It should be noted, however, that nearly complete oxygen exclusion can be obtained if inert gas is added to a sealed mine only during periods of atmospheric pressure increase. A positive internal pressure would not be necessary during these periods as it is necessary only to assure that the mine

pressure never drops below atmospheric pressure. Here again, the possibility of applying such a technique to successive sections of an active mine should be considered. On abandonment, it might be necessary to use inert gas only in portions of the mine near the outcrop or having thin confining overburden.

Mine Flooding. The flooding of a mine is the most singularly effective method for stopping the formation of iron sulfate and sulfuric acid. Mine breathing is eliminated, since there is no semi-confined gas volume, and the aqueous barrier eliminates significant oxygen transport by diffusion. In the ideal case, all points of entry to a mine could be sealed with bulkhead seals, and the mine, or a portion thereof, simply allowed to fill with water. The concept and development of hydraulic bulkheads is not new, and has been used in mining practice for some time. Garcia and Cassidy[57] reported in 1938 on their use in Illinois mines. Interviews with mining engineers show that internal sealing was in use in Ohio in the 1930's, and probably the methods were used widely elsewhere. Bulkheads are currently used in active mines to stem the flow from abandoned areas, and recent Federal Water Quality Administration contracts have dealt with the remote placement of seals by use of bags and by other techniques such as grouting and self-sealing limestone. (58,59).

In the case of below-drainage mines, flooding on abandonment is a likely possibility, and it would be well to plan a mining operation so as to make this feasible from an engineering standpoint. Above-drainage underground mines, on the other hand, present a more difficult problem. In planning new above-drainage mining operations, attention should be given to the possibility of flooding part or all of the mine on abandonment, with the placement of a minimum number of bulkhead seals. Such approaches should be considered as mining down slope, leaving several hundred feet of outcrop coal, and making all new mines shaft mines. The topography and geological structure of an area are the major factors in assessing the feasibility of such approaches.

In the case of existing abandoned underground operations, a careful investigation of the feasibility of mine flooding is a necessary prerequisite to planning an at-source abatement program. Due consideration must be given to the ability of the mine to hold water, the number of seals necessary to flood a significant portion of the mine, and the capacity of the seals and the mine itself to withstand the hydraulic heads which would be encountered. While severe outcrop leakage problems will make flooding impractical in many instances, outcrop sealing techniques such as grouting, lime and limestone sealing, and the application of sodium silicate gels and other materials may be practical in certain instances. The in situ precipitation of materials which may be of value in sealing leakage areas is currently under investigation.[60]

In Pennsylvania the Department of Mines and Minerals, working with Gwin Engineers, Inc.,[61,62] designed and is installing concrete seals in mine openings of difficult or dangerous access in the Moraine

State Park, Pennsylvania. The deep mine seals employed feature the injection of retaining bulkheads of free flowing or blown aggregate at two points in the main entry. The aggregate bulkheads are injected with grout, and the seal is completed by pressure grouting the intervening space and the outcrop on both sides of the seal. The deep mine sealing program at this location was seventy percent complete at the end of 1969.[62] At that time, the deep mine sealing program had shown a 76 percent improvement in water quality, reducing deep mine effluent acid from 96,000 pounds (July-December, 1967) to 23,000 pounds (July-December, 1969). Of the 23,000 pounds reported for the latter half of 1969, 9000 pounds were produced from mines which had had no reclamation work.

The remote placement of seals utilized at the Moraine State Park would appear to represent a sound approach except for possible settling into the floor or erosion of the floor beneath the seal over a period of time. Techniques have been devised to prepare an adequate base by remote methods. Actually, it is not known just what effect a load will have on the altered clay floor. It is possible that pressure grouting into and against the rib section may give sufficient lateral and vertical integrity to preclude problems associated with weak base materials. Outcrop leakage adjacent to the seal must be treated by a secondary grouting system to produce either a grout curtain or to create an integral monolithic body in the adjacent unstable area.

Bulkheads, even if they are found to be unable to completely flood the mining void, may well produce an effective seal in the area that they do hydraulically influence, and they might be effectively used in conjunction with carefully placed air seals. The optimum method of construction will vary widely with the characteristics of individual sites, with cost being a major consideration. Often, the expense of clearing the portal prior to building a seal is the largest single item in the total seal cost.

Control of Flushing of Acid Products from Areas of Pyrite Oxidation

The concept of water diversion is an approach which falls in the category of product transport control, as opposed to reactant transport control. In any type of pyritic system, it is evident that if the system can be hydraulically isolated so that no water leaves the system, then no drainage is produced even though pyrite oxidation may continue with the build-up of products in the system. In the case of above-drainage underground mines, in many parts of Appalachia the fall of ground water levels during the summer and autumn represents an example of natural seasonal water diversion, and the rise of ground water levels during the winter and spring results in a flushing out of accumulated acid products. In the same sense, drainage diversion may slow the rate of product release, but unless all water entry to and drainage from the system can be eliminated, the system drainage may ultimately reach a new

equilibrium, lower in flow rate, but proportionally higher in acid products. That is, the rate of acid product release may eventually attain the same level as before drainage diversion, with the only difference being that the volume of drainage is less. Depending on the structure of a given mine, it may also be that drainage diversion will effectively isolate certain areas, so that acid output from the total system will be lowered. It is potentially significant to note that an unexpected flush of water through a system which has been accumulating oxidation products will inevitably produce a flow of concentrated acid which could impose a serious shock loading on the receiving stream.

A novel approach to drainage diversion which has been proposed by Ahmed[63] is the concept of dewatering mines by using wells to pull down the water table. While the effect would probably be similar to more conventional drainage diversion practices, this concept might be applicable to a wider range of situations.

Existing field data are too incomplete at this time to allow any generalizations on the long-term effect of drainage diversion in underground workings. A conservative approach would indicate that while drainage diversion may provide temporary relief, and might therefore be very applicable to the control of acid release in sections of working mines, continuing control after abandonment will ultimately depend on oxygen transport control.

Reaction Kinetics Control

Inhibition of the Chemical Oxidation of Pyrite

The concept of applying inhibitors to the reactive pyrite surface has received moderate attention for a rather long period of time, with no indication of major success in the field. Barnes and Romberger[16] discuss the principles of inhibition or passivation, and conclude that this approach is impractical because of the probable necessity of high passivating reagent concentration, the difficulties in applying such agents to the reactive pyrite, and the continuous exposure of new pyrite by caving and slumping. If further work is done in this area, attention should be given not only to the types of inhibitors which might be applied, but also to the means of application. In the case of refuse and spoil piles, where only the pyritic materials in the first few feet below the surface will be significantly exposed to oxygen, it is conceivable that inhibitory agents could be effectively applied in liquid solution. On the other hand, this will not be possible in the case of underground mines. Even if access to all parts of an abandoned mine were possible, liquid applications to the walls and roof would not reach pyrite exposed along cracks and joints behind these surfaces. In the case of operating mines, the continuous application of an inhibitor might be feasible, although the expense and useful life of such applications has not been thoroughly investigated. It is more likely that inhibitory agents for abandoned underground mines would have to be applied in the

vapor phase, and would necessarily consist of volatile compounds. An abstract by Bloom et al.[64] reports that low molecular weight silane (SiH_4) derivatives are potential volatile inhibitors, although the writers of this report do not know of any field experiments to date.

Inhibition of Biological Catalysis of Pyrite Oxidation

The role of biological catalysis in increasing the rate of pyrite oxidation is still a major question in the understanding of acid mine drainage formation. In the laboratory, the presence of iron-oxidizing autotrophs in significant numbers has caused increases in pyrite oxidation rate by factors of 50 or more.[5,27,38] Recent reports[5,65] have given data on the environmental conditions under which microbial catalysis might be expected. However, we cannot state with assurance that microbial activity exerts a significant effect on pyrite oxidation rates in natural systems. The total pyrite oxidation rate is the sum of the rate due to chemical oxidation by oxygen, and the rate due to the activity of microorganisms. While the kinetics of the chemical rate are fairly well known, the rate due to microorganisms will be a function of the microbial population and the specific activity per microbial cell. Cell activity is a function of pH, oxygen concentration, and the availability of microbial nutrients such as nitrogen and carbon dioxide. Until more is known about these functional relationships, and until the environment at the pyrite surface in natural systems is described more fully, the role of bacterial catalysis in natural systems cannot be fully assessed. The following points, although insufficient to give a complete definition of the significance of bacterial catalysis, should be borne in mind in any consideration of bacterial activity:

(a) Wild strains of Ferrobacillus-Thiobacillus species grow readily in systems containing only pyrite and water, reach a maximum population usually on the order of 10^8 cells/ml, and appear to tolerate pH values down to about pH 1.2. The maximum rate of oxygen utilization by these organisms is on the order of 10^{-7} µg O_2/cell-hr.

(b) As mentioned in Sections VI and VII, a possible catalytic role of these organisms could be through the oxidation of Fe^{+2} to Fe^{+3} in solution, thereby making Fe^{+3} available to oxidize pyrite. The results of Lau[65] indicate that this is indeed the predominant mechanism. Whether the rate of pyrite oxidation by Fe^{+3} is greater than the rate of pyrite oxidation by O_2 will depend on the relative concentrations of Fe^{+2}, Fe^{+3} and O_2 at the pyrite surface.

(c) In view of the fact that the pyrite cannot be submerged in water without limiting O_2 transport which is required for both chemical and microbial oxidation, then there is a limit on how much water can surround the pyrite and still allow the pyrite to oxidize. This restriction on

water volume per unit area of pyrite places a restriction on the number of organisms the system can contain, and hence, on the rate of oxidation by the total microbial population. Also, a low water volume to pyrite area ratio will cause a rapid decrease in pH as the oxidation proceeds, which may inactivate any organisms in close proximity to the pyrite.

(d) The specific location in the system where microorganisms oxidize Fe^{+2} is of prime importance in determining whether the organisms exert any catalytic effect on pyrite oxidation itself. If the Fe^{+2} is flushed away from the pyrite before it is oxidized to Fe^{+3} by the microorganisms, then unless this Fe^{+3} is recycled back to the pyrite, or comes in contact with other pyrite further down the flow path, there will be no microbial catalysis of pyrite oxidation.

In other words, under the assumptions of paragraph (b) above, there may be significant microbial catalysis of iron oxidation, with little or no effect on the pyrite oxidation rate. Although autotrophic organisms are observed in mine drainage and in drainage impoundments, it cannot be readily determined whether the organisms grew in close proximity to pyrite, or grew on Fe^{+2} after it was flushed away from the pyrite. Only in the former case will there be microbial catalysis of the pyrite oxidation rate. It should be noted that acid drainage flowing through pools on the floor of underground mines may provide sufficient detention times for the growth of bacteria to high concentrations. In such a situation, bacteria will be observed in the drainage, and the Fe^{+3}/Fe^{+2} ratio in the drainage will be high, but there may still be little or no bacterial activity at the sites of pyrite oxidation. Existing field data are not sufficient to allow a firm evaluation of this point.

In the opinions of the authors of this section, significant bacterial catalysis of pyrite oxidation in underground mines is unlikely. If bacterial activity is significant, then bactericides might be a means of positive control. Because of necessity of bringing the bactericidal agent into contact with the oxidizing pyrite, which is generally not exposed at the coal face but is buried some distance back of the face, the agent will probably have to be applied as a vapor. At the time of this writing, the authors are aware of no field applications of bactericidal agents or inhibitors which have shown any sustained effects on acid drainage formation in underground mines.

MISCELLANEOUS

The preceding discussion of possible approaches to at-source abatement of pyrite oxidation and/or acid drainage from underground mines is predicated on the assumption that pyritic material remaining in the mine must be left in place. An alternative which might be economically feasible in some underground situations is that of stripping out the coal from the affected area, and employing normal strip mine abatement and reclamation procedures.

REFUSE AND SPOIL PILES

The technical problems associated with the abatement of pyrite oxidation in refuse and spoil piles are more straightforward than in the case of underground mines, largely because the reactive pyrite is readily accessible. As indicated in Section V, oxidation will be limited to the surface layers of the piles, and in the case of strip mining the placement of pyritic materials deep within the pile will eliminate the possibility of significant oxidation. The permanent flooding of pyritic materials in either refuse or spoil, where possible, will eliminate oxidation. Existing refuse piles, which represent perhaps the most difficult problem, may be quite large and are normally heavily loaded with pyritic material throughout the pile. In the case of both refuse piles and spoil banks with pyritic material exposed at the surface, there are three possibilities of abatement; i.e., (a) development of an oxygen transport barrier at the pile surface, (b) control of the reaction rate through either chemical inhibitors or bactericidal agents, and (c) prevention of water infiltration into the pile surface.

Mass Transport Control

Oxygen Available for Pyrite Oxidation

The establishment of a cover over exposed pyritic material immediately suggests the possibility of both artificial covers and natural vegetative covers. It is convenient to discuss these separately.

Artificial Cover. Any artificial cover which is waterproof will also exclude oxygen from the pyrite. Plastic films, bituminous concrete, and surface sealants such as lime and sodium silicate have all been suggested as possible cover materials; several types of applications are currently under investigation.[66-68] There is no doubt that an impermeable barrier will effectively do the multiple job of controlling oxygen availability, controlling erosion of the surface, and excluding water from the pile. Acid production will be essentially stopped, and with ground water replenishment also eliminated, acid seepage from the pile will gradually cease. The primary consideration, then, is one of initial cost and the cost of continuing maintenance. It is probable that

artificial covers will be economically attractive only in the case of short-term, temporary abatement projects.

Vegetative Cover. A vegetative cover has the attraction that is is potentially permanent and self-healing, as well as being more satisfactory from an aesthetic standpoint than artificial covers. It precludes, however, the possibility of complete elimination of either oxygen or water entry into the pile. Further, grading and surface drainage must be carefully designed to prevent erosion of the cover, and both spoil or refuse neutralization and the application of fertilizers would normally be required.

A vegetative cover might function in two basic ways; i.e., it might provide sufficient oxygen consumption capacity in the root zone and humus to prevent oxygen penetration to the buried pyritic material, or it might merely act as an erosion control device. If oxygen does penetrate the vegetative cover and reaches the buried pyritic material, the pyrite will eventually be oxidized, but no new pyrite will be exposed by erosion. The pyrite oxidation rate of such a system would gradually decay because of increasing diffusive resistances to oxygen transport as the reactive zone moves deeper into the pile. In any particular case, both mechanisms would be operative to some degree.

There is a lack of field data relating to the effectiveness of vegetative covers as a means of controlling acid production. However, the continued monitoring of the reclamation program near Elkins, West Virginia,[50] and current work by the Truax-Traer Coal Company near DuQuoin, Illinois,[66] are generating valuable data. Fundamentally, the behavior of any vegetative cover depends on the reactivity of the pyritic surface to be covered, the diffusivity of oxygen through any soil separating the pyrite from the atmosphere, and the oxygen-consuming capacity of the soil-humus layers. Good[7] estimated the average acid production rate of a 40-acre refuse pile in Illinois to be 4 to 5 tons of acidity (as $CaCO_3$) per day. Using this reactivity, and assuming a dry, granular soil, it would be necessary to cover pyritic material with more than 10 feet of soil to significantly limit pyrite oxidation by using the soil alone as a diffusion barrier. The presence of moisture in the soil decreases oxygen diffusivity, as does a decrease in grain size and porosity, with tightly packed, saturated clay being essentially impermeable. Because of wide variations in performance, soil covers less than 10-15 feet thick cannot be generally considered effective diffusion barriers. With the establishment of a vegetative cover, however, the use of a relatively thin soil cover over the pyritic material may be of considerable value, even though the soil layer itself might not be an effective diffusion barrier.

At the present time, it has been widely demonstrated that with proper fertilization and neutralization, grasses can often be readily grown directly on 'hot' spoil and on refuse containing high concentrations

of pyrite. Such plantings, however, should be observed for several seasons. If there is sufficient limestone in the neutralized material to essentially neutralize all the acidity which will ultimately be produced in the reactive surface layer (pyrite oxidation proceeds readily at alkaline pH values), then the root zone may never become acid, and the vegetation may survive indefinitely as long as ground water conditions do not allow acid to rise from below into the root zone. On the other hand, it is possible that a stand of grass planted on refuse would do well for a season or two, and then die when the available limestone is depleted by continuing acid formation. There is also the possibility that a sufficient oxygen-consuming layer might be developed rapidly enough that after a season or so, little oxygen penetrates to the pyrite, and it would not matter greatly whether the limestone were depleted or not. Definitive field data do not exist at this time on the evaluation of such direct-planting covers.

A second type of vegetative cover would be one in which the refuse (or acid spoil) is covered with a layer of sweet soil, with or without neutralization of the refuse or spoil before covering. In this case, there is no pyrite directly in the root zone, and the soil would become contaminated with acid only if acid salts are carried upward from the buried refuse by capillary rise. A layer of limestone at the surface of the refuse would provide temporary neutralization capacity to counteract this effect. Aside from this, the behavior of such a cover will be similar to a cover planted directly in neutralized refuse. That is, there will be some oxygen utilization in the humus and root zones, and some diffusive resistance to oxygen transport through the soil to the buried pyritic material. The amount of diffusive resistance offered by the soil will depend on the nature and degree of compaction of the soil, the moisture content, and the depth of the root zone. Generally speaking, it would appear that shallow-rooted perennial grasses would be ideally suited for vegetative covers.

While definitive field data on the effectiveness of shallow soil covers are not presently available, several projects[50,66,62] may provide such data in the near future. It should be recognized, however, that while survival of a vegetative cover controls erosion and eliminates exposure of new pyrite, it is not in itself an indication that pyrite oxidation has been stopped. Only sub-surface soil and gas samples can provide data for the estimation of pyrite oxidation rates. If the reaction has been stopped, acid products will eventually be flushed away from the pyritic material by infiltrating precipitation. This flushing effect may be quite slow, however, and it may require several years to indicate positive improvement. An analysis of subsurface gas samples for oxygen and carbon dioxide will yield direct information on the rate and extent of oxygen entry into the refuse or spoil layers, and can provide an immediate indication of the effect of any cover on pyrite oxidation rates. While data of this type are lacking at this time, such data are being generated.[66]

Reaction Kinetics Control

The concept of applying agents to refuse and spoil which will inhibit either chemical pyrite oxidation or microbially catalyzed pyrite oxidation is conceptually more attractive than in the case of underground mines. Agents can be added in liquid form by spraying directly on the surface. Aside from the ease of application, however, there are as many problems as for underground mines. Inhibitors of the chemical reaction which are effective at economic dosages have not been demonstrated under field conditions, and in any case, the problem of erosion would have to be solved separately.

Although many liquid agents have been studied which will inhibit the autotrophic bacteria suspected of having a rate-controlling effect on pyrite oxidation[69] (e.g., hexanoic acid and alkylbenzene sulfonate), again there are no confirming field data. Of more significance, however, is the fact that the magnitude of the effect of bacteria on total pyrite oxidation rates is subject to serious question. While a refuse or spoil pile appears to offer a far better environment for bacterial catalysis of pyrite oxidation than underground mines, the work of Lau[65] indicates that pyrite-to-water ratio will exert a limiting effect. In the opinions of the authors of this section, it is doubtful that the bacterial contribution to pyrite oxidation in refuse piles can exceed 50 per cent of the total pyrite oxidation rate. Further, as in the case of inhibition of the chemical reaction, erosion would have to be controlled separately. It is doubtful that reaction rate control, even if suitable inhibiting agents become available, will be feasible for any other than temporary alleviation applications.

Product Transport Control

As an introduction to this section, it is helpful to visualize the condition of a refuse or spoil pile which has stood exposed to the elements for a number of years. Raindrop impact and storm runoff washes fines (clay, etc.) from the outer mantle of the pile, exposing any pyritic material present to oxygen. Pyrite oxidation proceeds more or less continuously, with a buildup of acid products near the site of oxidation. During a rain (or period of snow melt) some of the acidity is carried away in surface runoff, and the remainder, perhaps as much as 30-40 per cent, is carried into the pile with the infiltrating precipitation. A ground water pool may build up within the pile, and the water in the pile will either seep out around the perimeter, or seep into the original ground below the pile. Consequently, once a pile has aged, it is more or less completely permeated with acid and acid salts.

Taking this model pile as an example, let us assume that a vegetative cover has been developed on the pile, and that it is successful in stopping pyrite oxidation. Infiltrating precipitation may require many years to clear the pile interior of previously formed acid products. This effect will have to be accounted for in efforts to evaluate abatement

techniques on refuse and spoil piles. Further, residual acid groundwater seepage occuring after a vegetative cover has been established may cause additional problems in that such seepage might emerge at the surface near the toe of the revegetated slopes. If the vegetative cover at the toe of a steep slope is destroyed by acid seepage, subsequent erosion may damage or destroy the remainder of the cover and re-expose pyrite to oxidation. In anticipation of such problems, subsurface toe drains are being employed at the refuse pile study in Illinois.[66]

Artifical covers, unlike vegetative covers, hold the possibility of completely excluding precipitation from entry into the pile. If this is done, then acid products will be retained in the refuse or spoil, unless the terrain and hydrology of the system are such as to allow ground or surface water to enter the pile from adjacent areas.

In general, the concept of water diversion in the case of refuse piles and spoil banks is more straightforward than in the case of underground mines. First, there is the real possibility of completely excluding direct precipitation entry by the construction of an impermeable surface seal. In many systems, this will be the sole point of water entry. Second, the cover, if truly impermeable, will also shut off oxygen entry to the pyrite and completely stop pyrite oxidation. Cost and long-term durability information for impermeable seal materials is not generally available.

A final subject which relates to acid product transport control and water diversion is that of grading the side slopes. It is a practice in some areas to grade a refuse pile to a steep slope in order to reduce the time runoff water is in contact with the refuse surface. While such a practice might decrease infiltration to some degree, it will have no direct effect on pyrite oxidation rate, and the exposed pyrite will oxidize at essentially the same rate, whether the water runs off slowly or rapidly. Steep slopes will simply increase erosion and make it more difficult to establish and maintain a vegetative cover.

SECTION IX

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SECTION X

REFERENCES

1. Martin, E. J., and Hill, R. D., "Mine Drainage Research Program of the Federal Water Pollution Control Administration," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

2. Corps of Engineers, "Report For Development of Water Resources of Appalachia," Appendix C- Prevention of Water Pollution by Drainage from Mines, U. S. Army Corps of Engineers (1969).

3. Hill, R. D., "Mine Drainage Treatment, State of the Art and Research Needs," U. S. Department of the Interior, Federal Water Pollution Control Administration, Cincinnati, Ohio, (1968).

4. Mine Drainage Abstracts, prepared annually by Bituminous Coal Research, Inc., Monroeville, Pa.

5. Smith, E. E., and Shumate, K. S., "Sulfide to Reaction Mechanism," Water Pollution Control Research Series, Report No. 14010 FPS - DAST-40, U. S. Dept. Interior, FWPCA, (Feb., 1970).

6. Shumate, K. S., and Smith, E. E., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

7. Good, D. M., et al. "The Relation of Refuse Pile Hydrology to Acid Production," Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

8. Garrels, R. M., and Christ, C. L., Solutions, Minerals, and Equilibria, Harper & Row, New York, (1965).

9. Sato, M., "Oxidation of Sulfide Ore Bodies, I, Geochemical Environments in Terms of E_h and pH," Econ. Geology, 55 (1960), 928.

10. Sato, M., "Oxidation of Sulfide Ore Bodies, II, Oxidation Mechanisms of Sulfide Minerals at 25°C," Econ. Geology, 55 (1960), 1202.

11. Clark, C. S., "Oxidation of Coal Mine Pyrite," J. Sanitary Eng. Div. ASCE, 92 Proc. Paper 4802, (1966), 127.

12. Hem, J. D., "Restraints on Dissolved Ferrous Iron," U. S. Geological Survey, Water Supply Paper 1459-B, (1960).

13. Hem, J. D., and Cropper, W. H., "Survey of Ferrous-Ferric Chemical Equilibria and Redox Potentials," U. S. Geological Survey, Water Supply Paper 1459-A, (1959).

14. Barnes, E., and Clarke, F. E., "Geochemistry of Ground Water in Mine Drainage Problems," Professional Paper 473-A, Geological Survey, U. S. Department of Interior, (1964).

15. Singer, P. C., and Stumm, W., "Kinetics of the Oxidation of Ferrous Iron," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

16. Barnes, H. L., and Romberger, S. B., "Chemical Aspects of Acid Mine Drainage," J. Water Pollution Control Federation, 40 (1968), 371.

17. Braley, S. A., "Summary Report Mellon Institute Fellowship No. 326B," Mellon Institute of Industrial Research, (1954).

18. Burke, S. P., and Downs, R., "Oxidation of Pyritic Sulfur in Coal Mines," AIMME Trans., 130 (1938), 425.

19. Nelson, H. W., et al, "Oxidation of Pyritic Sulfur in Bituminous Coal," I. E. C., 25 (1933), 1355.

20. Morth, A. H., and Smith, E. E., "Kinetics of the Sulfide-to-Sulfate Reaction," Proceedings, 151st National Meeting, Am. Chem. Soc., Pittsburgh, Pa., (March, 1966).

21. Jutte, R. B.,Jr., "The Effect of Oxygen and Nitrogen in Aqueous Solution on the Kinetics of the Sulfide-to-Sulfate Reaction," M. S. Thesis, The Ohio State University, (1966).

22. Hougen, O. A., and Watson, K. M., Chemical Process Principles, Part III John Wiley & Sons, Inc., New York, (1947).

23. Smith, E. E.; Svanks, K.; and Shumate, K. S., "Sulfide-to-Sulfate Reaction Studies," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

24. Birle, J. D., "Sulfide to Sulfate Reaction Mechanism in Pyritic Materials," M. S. Thesis, The Ohio State University, (1963).

25. Stiles, David, Unpublished data, The Ohio State University.

26. Caruccio, F. T., "An Evaluation of Factors Affecting Acid Mine Drainage Production," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

27. Konecik, M. G., "The Biological Oxidation of Iron Pyrite," M. S. Thesis, The Ohio State University, (1965).

28. Garrels, R. M., and Thompson, M. E., "Oxidation of Pyrite by Iron Sulfate Solution," Am. J. Sc., 258-A (1960), 57.

29. Smith, E. E.; Svanks, K.; and Halko, E., "Aerobic-Anaerobic Oxidation of Pyrite," Proceedings, 157th National Meeting, Am. Chem. Soc., Fuel Sym., 13 No. 2, (April, 1969).

30. Dugan, P. R., and Lundgren, D. G., "Energy Supply for the Chemoautotrophic Ferrobacillus ferrooxidans," J. Bacteriol., 89 (1965), 825.

31. Lorenz, W. C., and Torpley, E. C., "Oxidation of Coal Mine Pyrites," R.I. 6247, U. S. Bureau of Mines, Washington, D.C., (1964).

32. Silverman, M. P., "Mechanism of Bacterial Pyrite Oxidation," J. Bacteriol., 94 No. 4 (1967), 1046.

33. Bailey, J. R., "Biological Oxidation of Pyrite," M. S. Thesis, The Ohio State University, (1968).

34. Dugan, P. R. and Randles, C. I., "The Microbial Flora of Acid Mine Water and its Relationship to Formation and Removal of Acid," Project Completion Report A-002-OHIO, to Office of Water Resources Research, USDI, (October, 1968).

35. Ivanov, M. V., "Microbiological Processes in the Formation of Sulfur Deposits, (1964), Trans. from Russian, 1968. Publ. Israel Program for Scientific Translations for U.S. Dept. Agr. and NSF., 298 pp.

36. Kelly, D. P., "Problems of the Autotrophic Micro-organisms," Sci. Prog. Oxf., 55 (1967), 35-51.

37. Peck, H. D., "Energy Coupling Mechanisms in Chemolithotrophic Bacteria," Ann. Rev. Microbial., 22 (1968), 489-518.

38. Silverman, M. P., and Ehrlich, H. L., "Microbial Formation and Degradation of Minerals," Adv. in Appl. Microbiol, 6 (1964), 153.

39. Riley, C. V., "Limnology of Acid Mine Water Impoundments," First Symposium on Acid Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1965).

40. Tubb, R. A., et al., "Potential of a Strip Mined Area for Fish and Wildlife Reclamation," Rpt. 2296, The Ohio State University Research Foundation, 84 pp.

41. Sokolova, G. A., and Karavaiko, G. I., "Physiology and Geochemical Activity of Thiobacilli," (1964). Trans. from Russian, 1968. Publ. Israel Program for Scientific Translations for U.S. Dept. Agr. and NSF., 283 pp.

42. Whitesell, L. B. Jr.; Huddleston, R. L.; and Allred, R. C., "The Microbiological Oxidation of Ferrous Iron in Mine Drainage Water," Paper presented at 157th National Meeting, Am. Chem. Soc., Minneapolis, Minnesota, (April, 1969).

43. Trudinger, P. A., "The Metabolism of Inorganic Sulfur Compounds by Thiobacilli," Review of Pure and Applied Chemistry, 17 (1967), 1-24.

44. Tuttle, J. H.; Dugan, P. R.; and Randles, C. I., "Microbial Sulfate Reduction and Its Potential Utility as an Acid Mine Water Pollution Abatement Procedure," Applied Microbiology, 17 (1969), 297-302.

45. Zawadzki, E. A., and Glenn, R. A., "Sulfide Treatment of Acid Mine Drainage," Summary Rept., Bituminous Coal Research, Monroeville, Pa., to FWPCA, (1968), 87 pp.

46. Shearer, R. E., and Everson, W. A., "Study of Bacteriophages in Controlling Acid Mine Water," First Symposium on Acid Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1965).

47. Shearer, R. E., et al, Everson, W. S., Mausteller, J. W., "Reduction of Acid Production in Coal Mines with Use of Viable Anti-bacterial Agents," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

48. Shearer, Robert E., and Everson, W. A., "Effect of Antibacterial Agents on Mine Drainages," Water Pollution Control Research Series, FWQA publication 14010 EGJ, (November, 1968).

49. Moebs, N. N., and Krickovic, S., "Air-Sealing Coal Mines to Reduce Water Pollution," Bureau of Mines Report No. RI7354, U. S. Dept. Interior, (March, 1970).

50. Hill, R. D., "Elkins Mine Drainage Pollution Control Demonstration Project," Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

51. Shumate, K. S., and Smith, E. E., "Development of a Natural Laboratory for the Study of Acid Mine Drainage Production," Second Symposium on Coal Mine Drainage Research, Mellon Inst., (May, 1968).

52. Moebs, N. M., "Mine Air Sealing: A Progress Report," Second Symposium on Coal Mine Drainage Research, Mellon Inst., (May, 1968).

53. Hill, R. D., "The Effectiveness of Mine Drainage Pollution Control Measures at Elkins, W. Va.," Proceedings, 157th Nat. Meeting, Am. Chem Soc., Division of Fuel Chem., 13, No. 2, (1969).

54. Black, A. S., Soil Plant Relationships, John Wiley and Sons, New York, (1968), 153-197.

55. Leitch, R. D., et al., U. S. Bureau of Mines Report, RI2994, (1930).

56. Rice, J. K., "The Use of Inert Gas to Eliminate Acid Production by Abandoned and Active Deep Mines," Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

57. Garcia, J. A., and Cassidy, S. M., "Bulkheads for Coal Mines," AIME Tech. Pub. No. 789, (1938).

58. Wenzel, R. W., "Feasibility Study on the Application of Various Grouting Agents, Techniques and Methods to the Abatement of Mine Drainage Pollution, Part IV," Halliburton Co., Draft Final Report to U. S. Dept. Interior, FWPCA, Monongahela River Mine Drainage Remedial Project, (1968).

59. Pollution Abatement through New Mine Sealing Techniques, FWQA Publication 14010 DMO, Washington, D.C., (1970).

60. Jones, J. B., and Ruggeri, S., "Abatement of Pollution from Abandoned Coal Mines by means of In-Situ Precipitation Techniques," Proceedings, 157th Nat. Meeting, Am. Chem Soc., Division of Fuel Chem., 13, No. 2, (1969).

61. Foreman, J. W., and Tarr, E. G., "Moraine State Park Mine Drainage Project," Second Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1968).

62. Foreman, J. W., "Evaluation of Pollution Abatement in Moraine State Park," Third Symposium on Coal Mine Drainage Research, Mellon Institute, Pittsburgh, Pa., (1970).

63. Ahmad, M. U., Ohio University, Athens, Ohio, Unpublished Communication, (1970).

64. Bloom, D. N., et al., Presentation at Am. Inst. Chem. Engrs. workshop; Industrial Process Design for Water Pollution Control, Houston, Texas, (April, 1969).

65. Lau, C. M., et al., "The Role of Bacteria in Pyrite Oxidation Kinetics", Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

66. Ramsey, J. P., "Control of Acid Drainage from Refuse Piles and Slurry Lagoons," Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

67. "Coal Refuse Binder," FWQA Project No. 14010 FOA, grant to Black, Sivalls, and Bryson, Inc., Pittsburgh, Pa., Grant period 3/70 to 8/70.

68. Walitt, A., et al., "Silicate Treatment of Coal Mine Refuse Piles," Third Symposium on Coal Mine Drainage Research, Mellon Institute, (May, 1970).

69. Tuttle, J. H., "Aspects of Iron and Sulfur Oxidations by the Chemoautotroph Thiobacillus ferrooxidans with Emphasis on Inhibition by Organic Compounds," Ph.D. Dissertation, The Ohio State University, (1969).

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KEY WORDS:

Acid mine water
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Pollution abatement
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The central theme of this report pertains to at-source control of pyrite oxidation. The current level of knowledge of acid mine drainage formation is critically reviewed, with emphasis on reaction kinetics and reactant and product transport. A reaction system model is developed which provides a conceptual framework for subsequent discussion dealing specifically with the physical, chemical, and biological characteristics of pyritic systems encountered in mining situations. Practical considerations of at-source control of acid mine drainage formation in underground mines, spoil banks, and refuse piles are presented in the final section of the report. Deficiencies in current knowledge which are brought out by this report include: Descriptions of the physical environment existing at pyrite oxidation sites in natural systems are far more incomplete than the current understanding

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